PB90-166406

# PROPOSED TREATMENT TECHNOLOGY BACKGROUND DOCUMENT

(U.S.) Environmental Protection Agency
Washington, D.C.

Nov 89

U.S. Department of Commerce
National Technical Information Service
NTIS

50272-101

| | | | |
|---|---|---|---|
| REPORT DOCUMENTATION PAGE | 1. REPORT NO.<br>EPA/530-SW-90-012B | 2. | 3.<br>**PB90-166406** |

4. Title and Subtitle
PROPOSED TREATMENT TECHNOLOGY BACKGROUND DOCUMENT (3RD 3RDS)

5. Report Date
NOVEMBER 1989

6.

7. Author(s)
BERLOW/ROSENGRANT

8. Performing Organization Rept. No

9. Performing Organization Name and Address

U.S. EPA
Office of Solid Waste
401 M. Street SW
Washington, DC 20460

10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.
(C)
(G)

12. Sponsoring Organization Name and Address

13. Type of Report & Period Covered
BACK. DOCU. - 11/89

14.

15. Supplementary Notes

16. Abstract (Limit: 200 words)

This document provides a discussion of the purposes and contents of each of the various elements presented in each technology section. This document explains what information is provided in each technology subsection, how the Agency intends to use this information as part of its BDAT program, and how the Agency intends to modify the treatment technology discussions as more treatment data and information become available.

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms

c. COSATI Field/Group

| | | |
|---|---|---|
| 18. Availability Statement<br>RELEASE UNLIMITED | 19. Security Class (This Report)<br>UNCLASSIFIED | 21. No. of Pages<br>0 |
| | 20. Security Class (This Page)<br>UNCLASSIFIED | 22. Price<br>0 |

(See ANSI-Z39.18)

OPTIONAL FORM 272 (4-77)
(Formerly NTIS-35)

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL INFORMATION SERVICE
SPRINGFIELD, VA. 22161

#00

#01 PB90-166406

#02 Field 68C

#03 U057148

#23 Descriptors: *Waste treatment, *Hazardous materials, Thermal treatment, Retorting, Ion exchanging, Stripping(Distillation), Performance evaluation, Design criteria, Aerobic processes, Activated sludge process, Materials recovery, Reduction, Leaching, Oxidation, Precipitation(Chemistry), Lagoons(Ponds), Trickling filtration, Physical properties, Solvent extraction.

#25 Identifiers: *Best technology, *Technology utilization, *Pollution regulations, *Resource Conservation and Recovery Act, *Waste utilization, Rotating biological contactors, US EPA, Biological industrial waste treatment, Fuel substitutes, Refuse derived fuels, Incineration.

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#30 0

D.M.

CONTROL NUMBER: 057148

BATCH NUMBER:

MGT. CD.

| AN | RV | KY | VR | ED |
|---|---|---|---|---|
| C | | | | |

ACCESSION NUMBER: PB90-166406

03A) ANN GRA WGA DB

03G) GRAPHICS

30A) 0

0 N/A
1 Am-r
2 R
3 T
4 FOR
5 For-T
6 For-R

02S) SUBJECT CATEGORIES

68C

23D) DESCRIPTORS

*Waste treatment,
*Hazardous materials,
Thermal treatment,
~~Filtration~~,
Retorting,
Ion exchanging
Stripping (Distillation),
Performance evaluation,
Design criteria,
Aerobic processes,
Activated sludge process,

Materials recovery
Reduction,
Leaching,
Oxidation,
Precipitation (Chemistry),
Lagoons (Ponds),
Trickling filtration,
Physical properties,
~~Distillation~~,
Solvent extraction.

25I) IDENTIFIERS

*Best technology,
*Technology utilization,
*Pollution regulations
*Resource Conservation and Recovery Act,
*Waste utilization,
Rotating biological contactors,
US EPA
Biological industrial waste treatment,

Fuel substitutes,
Refuse derived fuels,
Incineration.

27A) ABSTRACT

PAGES

PB90-166398
PB89-221410

BOS ☑ 2
NONE ☐
BELOW ☐

EPA | 530-SW-90-012B

# PROPOSED

# TREATMENT TECHNOLOGY BACKGROUND DOCUMENT

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November 1989

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# EXECUTIVE SUMMARY

## INTRODUCTION

This section of the treatment technology document provides a discussion of the purpose and contents of each of the various elements presented in each technology section. Specifically, this section explains what information is provided in each technology subsection, how the Agency intends to use this information as part of its BDAT program, and, when applicable, how the Agency intends to modify the treatment technology discussions as more treatment data and information becomes available. Below are discussions of the following elements of the technology write-ups: applicability, underlying principles of operation, description of the technology, waste characteristics affecting performance, and design and operating parameters.

### 1. Applicability

(a) Information Provided. This applicability section contains information on the general application of the treatment technology to various wastes. EPA's analysis of applicability is performed in consideration of the parameters and constituents known to affect treatment selection. That is, in order to identify whether a treatment technology was applicable to any particular waste stream, the Agency considered all parameters and characteristics associated with a hazardous waste that could affect the selection of treatment technology. EPA uses the acronym PATS for these parameters (i.e., parameters affecting treating selection).

EPA's list of parameters affecting treatment selection (PATS), shown in Table 1-1, identifies all known constituents and parameters that are needed to select a technology or technology train for a given waste.

Table 1 List of Parameters Affecting Treatment Selection

---

- BDAT metals
- BDAT organics
- Other BDAT constituents (sulfides and fluorides)
- Biological oxygen demand (BOD)
- BTU content
- Complexed metals
- Cyanide
- Filterable solids
- Oil and grease content
- pH
- Total organic carbon (TOC)
- Total organic halides (TOX)
- Viscosity
- Water content
- Selectivity value
- Ash fusion temperature

---

It is important to point out that in developing this list, EPA's goal was to determine the demonstrated technology that would best treat all of the constituents in the waste (i.e., achieve the lowest concentration in the residual). Accordingly, EPA will add components to the treatment train as long as they are demonstrated and will achieve statistically significant reduction in the concentrations of the constituents. (Note: the statistical analysis that the Agency uses to determine whether a significant reduction in constituents has occurred is referred to as Analysis of Variance (ANOVA).

(b) EPA's Use of this Information. EPA uses the PATS as the basis for making decisions regarding whether a particular technology is "demonstrated" for a particular waste. The Agency is performing treatment tests on specific wastes to "demonstrate" the treatment of the waste using the technology, develop treatment standards, and to set the criteria by which other wastes can be regulated using the demonstrated technology.

The PATS analysis will sometimes show that several technologies are applicable for treating the waste. EPA will prioritize these technologies based on its analysis of available data and information regarding the effectiveness of the various technologies. For organics, EPA's preference will be technologies that recover or destroy the compounds; for metals, the Agency's preference will be technologies that result in recovery of the metals.

In some instances, analysis of a particular parameter will not be possible or would be meaningless with regard to selecting a treatment system (for example, a percent water analysis for a U or P waste spill resulting in contaminated soil).

(c) Use of New Data and Information. As data become available either from industry or through EPA's BDAT data collection program, EPA will modify the PATS analysis to further refine specific concentration ranges for which various technologies can handle various parameters.

## 2. Underlying Principles of Operation

(a) Information Provided. For each treatment technology EPA provides the fundamental theory of operation of the technology. This section is not meant to provide a detailed discussion on the specific complex physical, chemical, or biological mechanisms by which treatment occurs. Instead, the discussion describes the mechanisms involved so that one can understand what characteristics can affect the performance of the technology. For example, the underlying principle of chemical precipitation is that metals in wastewater are removed by adding a treatment chemical to form a metal precipitate which is generally insoluble and thereby settles out of solution. Formation of the precipitate and the settling mechanism are the principles controlling technology performance.

(b) Use of Information Provided. The theory of operation is necessary as the precursor to analyzing which waste characteristics can affect the performance of a given treatment technology. That is, the principles of treatment operation are used as the rationale and basis upon which the Agency determines what waste characteristics can affect performance. Accordingly, waste characteristics affecting performance (WCAPs) which are discussed below, must be understood from the standpoint of how each waste characteristic inhibits or interferes with the fundamental operation of the treatment technology.

## 3. Description of the Treatment Process

**Information Provided and Use.** This section provides a brief description of the principal components of a treatment technology. It is intended to provide a basic understanding of the equipment used and the treatment sequence. This presentation serves to relate the discussion on underlying principles of operation with the later discussion of the design and operating parameters important to effective waste treatment. Simplified block diagrams are provided in this section. The information presented is general in nature to avoid attempting to show all potential combinations and permutations that are possible in describing a particular technology.

## 4. Waste Characteristics Affecting Performance (WCAP)

(a) **Information Provided.** The WCAP are based on the underlying principles of the treatment technology. For example, the underlying principle of chemical precipitation, presented above, is formation of the insoluble metal precipitate and the settling of the precipitate out of solution. WCAP for this technology are those parameters which affect the chemical reaction of the metal compound or the solubility of the metal precipitate (i.e., formation), and/or affect the ability of the precipitated compound to settle. The WCAPs include: (a) the concentration and type of metals, (b) the concentration of total dissolved solids, (c) the concentration of complexing agents, and (d) the concentrations of oil and grease. The first 3 parameters can affect precipitate formation and the last parameter can inhibit settling.

EPA's selection of WCAP's for the various treatment systems will be based on a literature review, as well as information obtained during plant sampling visits that test the treatment technology. EPA is aware that in some cases analytical methods are not available to measure the specific waste characteristics that affect treatment. In such instances, EPA will measure the parameter that most closely approximates the actual parameter of concern. For example, a WCAP for steam stripping is the relative volatility of a component. Because relative volatility cannot be measured, EPA uses boiling point as the best measure of assessing the WCAP of relative volatility.

The analysis of waste characteristics affecting performance is conducted where EPA already has determined from a PATS analysis that an untested waste could use the same BDAT technology as another waste for which treatment performance data are available. The WCAP analysis is then used to determine whether the treatment standard from the tested waste can be transferred to the untested waste. Simply stated, this analysis compares, for two separate wastes, the characteristics that affect the level of treatment that can be achieved. Where this comparison shows that the untested waste can be treated as well or better, the Agency will transfer the treatment standards to the untested wastes.

For example, for wastes that can be treated using chemical precipitation, if the Agency tests a waste containing lead at a given level, it will transfer the treatment standards developed from the test to a second lead-containing waste, if the second waste meets the following WCAP-based conditions:

- the lead concentration is similar to the tested waste,
- the second waste has a lower total dissolved solids level,

- the concentration and type of other metals is similar to the tested waste, and
- the untested waste has a concentration of oil and grease similar to or less than the tested waste.

(b) Use of Information Provided. In applying the WCAP analyses, it is important to remember that the technology itself, and the associated design and operating conditions, are fixed (i.e., they are fixed at the values that existed for the already tested waste). EPA does not assume that, where WCAPs for the untested waste show that it would be significantly harder to treat, the addition of another treatment component or a change in design and operating conditions will result in the untested waste achieving the same performance as the previously tested waste. EPA is aware that modifying the treatment system or operating conditions could result in similar treatment. However, the Agency is not certain, without demonstrating through testing, that treatment levels associated with BDAT standards (normally in the low part (<10) per million or part per billion range) can be achieved by simply changing treatment conditions. Accordingly, EPA will be very cautious in its decisions to transfer treatment standards where the WCAP analysis shows that treatment modifications are needed from the previously tested waste.

(c) Use of New Data and Information. In developing the WCAPs for the various treatment technologies, EPA found little and, in some cases, no information on the relative importance of the various WCAPs for a given technology (i.e., which waste characteristics have the most significant impact on treatment performance). Where information was available with regard to the specific WCAPs which are important when assessing the performance of a particular technology, EPA was unable to find any supporting data which would quantify the relative impact of each of the WCAPs on treatment performance.

As data become available either from industry or through EPA's BDAT data collection program, EPA may modify the WCAPs analysis to further refine the parameters identified as affecting treatment technology performance. As noted above, before it adopts a new WCAP, the Agency must understand how the parameters affect treatment relative to the underlying principles of operation.

## 5. Design and Operating Data

(a) Information Provided and Use. EPA will use design and operating information in several ways. First, this information is used, in conjunction with the Agency's BDAT data collection program, in determining whether a particular treatment system is well designed. That is, the Agency assesses design data prior to determining whether to test a particular piece of equipment or treatment train for potential use in the development of BDAT treatment standards. EPA obtains operating data during the course of an Agency sponsored treatment test to ensure the treatment system is well-operated. Secondly, EPA will expect facilities to provide the appropriate design and operating data when submitting treatment data to be considered in the development of the BDAT treatment standards. Again, this data will be assessed by the Agency to determine if the treatment system was well-designed and operated. Finally, EPA will require facilities petitioning for a treatment variance to submit the plant's design values and the operating data during the time of the treatment period to ensure the treatment system was well designed and operated.

# 1. AEROBIC BIOLOGICAL TREATMENT

## 1.1 Applicability

Aerobic biological treatment is a treatment technology applicable to wastewaters containing biodegradable organic constituents. Four of the most common aerobic biological treatment processes are (a) activated sludge, (b) aerated lagoon, (c) trickling filter, and (d) rotating biological contactor (RBC). The activated sludge and aerated lagoon processes are suspended-growth processes in which microorganisms are maintained in suspension with the liquid. The trickling filter and the RBC are attached-growth processes in which microorganisms grow on any inert medium such as rocks, slag, or specifically designed ceramic or plastic materials. This section discusses these four processes as well as the powdered activated carbon (PAC) adsorption process, which is a variation of the activated sludge treatment.

## 1.2 Underlying Principles of Operation

The basic principal of operation for aerobic biological treatment processes is that living, oxygen-requiring microorganisms decompose organic constituents into carbon dioxide, water, nitrates, sulfates, simpler low molecular weight organic byproducts, and cellular biomass. Wastes that can be degraded by a given species or genus of organisms may be very limited. A mixture of organisms may be required to achieve effective treatment, especially for wastes containing mixtures of organic compounds. Nutrients such as nitrogen and phosphorus are also required to aid in the biodegradation process.

The aerobic biodegradation process can be represented by the following generic equation:

$$C_x H_y + O_2 \xrightarrow[\text{nutrients}]{\text{microorganisms}} H_2O + CO_2 + \text{cellular biomass.}$$

Microorganisms produce enzymes that catalyze the biodegradation reactions, degrading the organic waste to obtain energy for cell metabolism and cell growth.

Aerobic biological treatment of wastewaters containing organic constituents results in the net accumulation of a biomass of expired microorganisms consisting mainly of cell protein. However, the cellular biomass or sludges may also contain entrained constituents from the wastewater or partially degraded constituents. These sludges must be periodically removed (wasted) to maintain proper operation of the aerobic biological treatment system.

## 1.3 Description of Aerobic Biological Treatment Processes

### 1.3.1 Activated Sludge

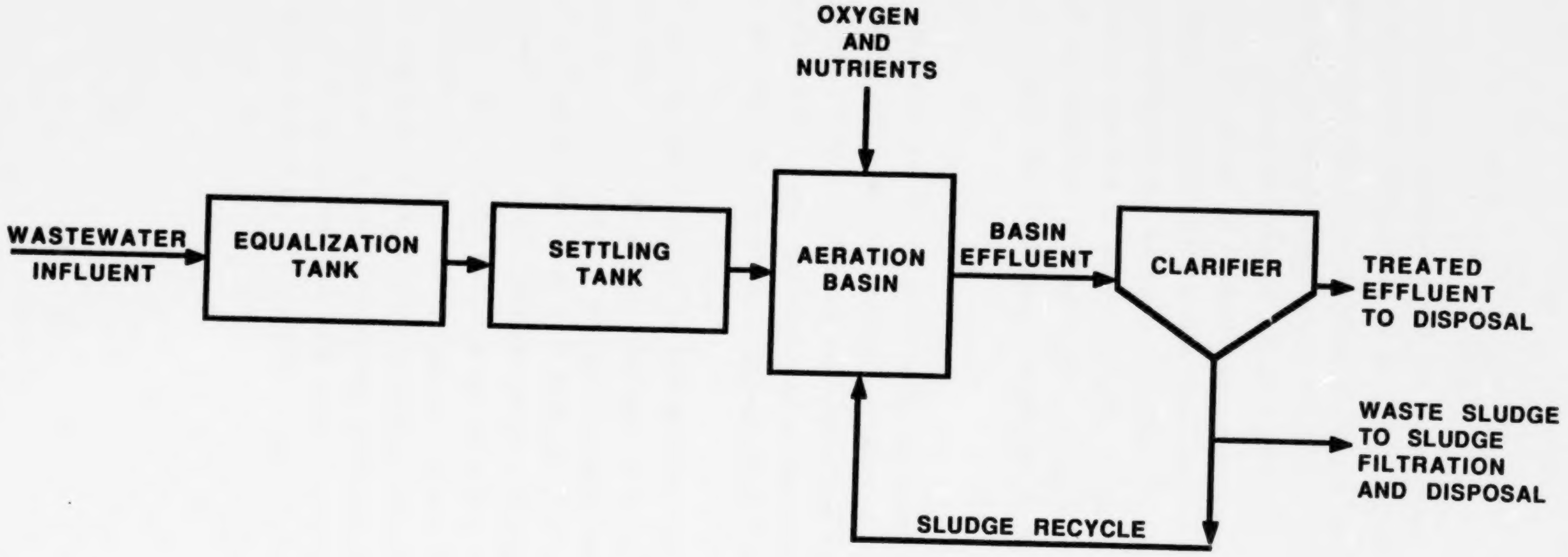
The activated sludge process is currently the most widely used biological treatment process. This is partly the result of the fact that recirculation of the biomass, which is an integral part of the process, allows microorganisms to adapt to changes in wastewater composition with a relatively short acclimation time and also allows a greater degree of control over the acclimated bacterial population.

An activated sludge system consists of an equalization basin, a settling tank, an aeration basin, a clarifier, and a sludge recycle line. Wastewater is homogenized in an equalization basin to reduce variations in the feed, which may cause process upsets of the microorganisms and diminish treatment efficiency. Settleable solids are then removed in a settling tank.

Next wastewater enters an aeration basin, where an aerobic bacterial population is maintained in suspension and oxygen, as well as nutrients, is provided. The contents of the basin are referred to as the mixed liquor. Oxygen is supplied to the aeration basin by mechanical or diffused aeration, which also aids in keeping the microbial population in suspension. The mixed liquor is continuously discharged from the aeration basin into a clarifier, where the biomass is separated from the treated wastewater. A portion of the biomass is recycled to the aeration basin to maintain an optimum concentration of acclimated microorganisms in the aeration basin. The remainder of the separated biomass is discharged or "wasted." The biomass may be further dewatered on sludge drying beds or by sludge filtration (which is further discussed in Section 21) prior to disposal. The clarified effluent is discharged. A schematic diagram of an activated sludge treatment system is shown in Figure 9-1.

The recycled biomass is referred to as activated sludge. The term "activated" is used because the biomass contains living and acclimated microorganisms that metabolize and assimilate organic material at a higher rate when returned to the aeration basin. This occurs because of the low food-to-microorganism ratio in the sludge from the clarifier.

An important variation on the activated sludge process is the Powdered Activated Carbon Treatment (PACT) process. This process offers a combined treatment and pretreatment system in which noncompatible and toxic constituents are adsorbed onto activated carbon, while microorganism-compatible waste remains in solution. Powdered activated carbon is added directly to the aeration basin of the activated sludge treatment system. Overall removal efficiency is improved because compounds that are not readily biodegradable or that are toxic to the microorganisms are adsorbed onto the surface of the powdered activated carbon. The carbon is removed from the wastewater in the clarifier along with the biological sludge. Usually, the activated carbon is recovered, regenerated, and recycled.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CLARIFIER
TREATED
EFFLUENT
TO DISPOSAL
WASTE SLUDGE
TO SLUDGE
FILTRATION
AND DISPOSAL
SLUDGE RECYCLE

Figure 1-1. Activated Sludge System.

### 1.3.2 Aerated Lagoon

Like an activated sludge system, an aerated lagoon is a suspended-growth process. The aerated lagoon system consists of a large pond or tank that is equipped with mechanical aerators to maintain an aerobic environment and to prevent settling of the suspended biomass. Initially, the population of microorganisms in an aerated lagoon is much lower than that in an activated sludge system because there is no sludge recycle. Therefore, a significantly longer residence time is required to achieve the same effluent quality. However, this longer residence time may be an advantage when complex organic chemicals are to be degraded. Also, the microorganisms in aerated lagoons are more resistant to process upsets caused by feed variations than those in activated sludge systems because of the larger tank volumes and longer residence times used. The effluent from the aerated lagoon may flow to a settling tank for removal of suspended solids. Alternatively, the mechanical aerators in the system may be shut off for a period of time to facilitate settling prior to discharge of the effluent. The settled solids are generally dewatered prior to disposal.

### 1.3.3 Trickling Filters

A trickling filter is an attached-growth biological treatment process. The system consists of an equalization basin, a settling tank, a filter medium, an influent wastewater distribution system, an under drain system, a clarifier, and a recirculation line. The filter medium consists of a bed of an inert material to which the microorganisms attach themselves and through which the wastewater is percolated. Rocks or synthetic material such as plastic rings and saddles are typically used as filter media. Following equalization and settling of settleable solids in the wastewater, it is distributed over the top of the filter medium by a rotating distribution arm or a fixed distributor system. The wastewater forms a thin layer as it flows downward through the filter and over the microorganism layer on the surface of the medium. As the distribution arm rotates, the microorganism layer is alternately exposed to a flow of wastewater and air. In the fixed distributor system, the wastewater flow is cycled on and off at a specified dosing rate to ensure that an adequate supply of oxygen is available to the microorganisms. Oxygen from air reaches the microorganisms through the void spaces in the media. Figure 1-2 presents a diagram of a trickling filter system.

A trickling filter system is typically used as a roughing filter to reduce the organic loading on a downstream activated sludge process. Trickling filters can be used for the treatment of wastewaters that could potentially produce "bulking" sludge (i.e., a sludge with poor settling characteristics and poor compactability in an activated sludge process) because the microbial solids that slough off the trickling filter medium are relatively dense and can be readily removed in a clarifier.

### 1.3.4 Rotating Biological Contactor (RBC)

A rotating biological contactor (RBC) consists of a series of closely spaced, parallel disks that are rotated at an average rate of 2 to 5 revolutions per minute while submerged to 40 percent of their diameters in a contact tank containing wastewater. The disks are constructed of polystyrene, polyvinyl chloride, or similar materials. Each disk is covered with a biological slime that degrades dissolved organic constituents present in the wastewater. As the disk is rotated out of the tank, it carries a film of the wastewater into the air, where oxygen is available for aerobic biological decomposition. As excess biomass is produced, it sloughs off the disk and is separated from the treated effluent in a clarifier. The sloughing off process is similar to that which occurs in a trickling filter. There is no recycle of sludges or recirculation of treated effluent in an RBC process. Several RBCs are

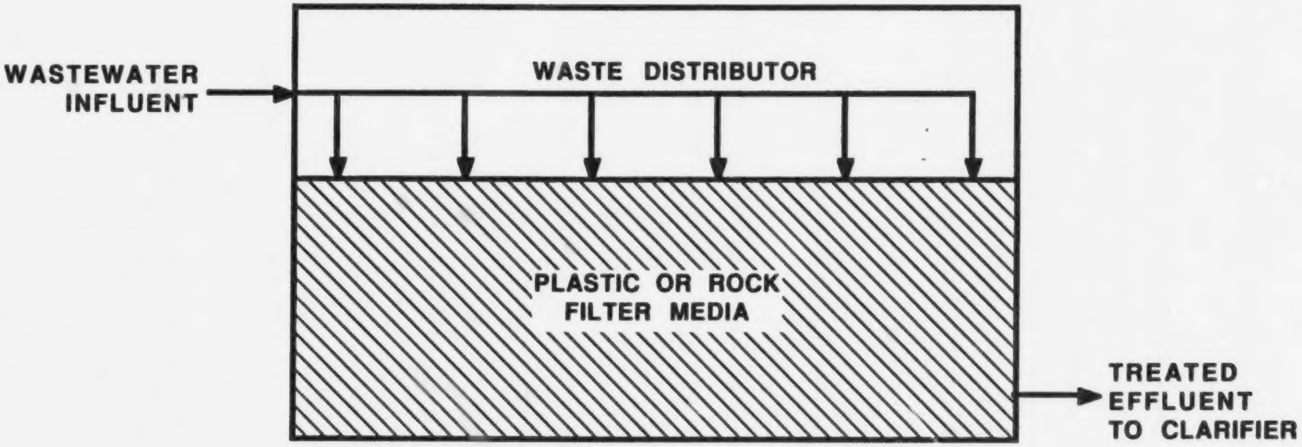
WASTEWATER INFLUENT
WASTE DISTRIBUTOR
PLASTIC OR ROCK FILTER MEDIA
TREATED EFFLUENT TO CLARIFIER

Figure 1-2. Trickling Filter System.

often operated in series, with the effluent from the last RBC being discharged. Biological solids are usually dewatered prior to disposal.

## 1.4 Waste Characteristics Affecting Performance (WCAPs).

In determining whether aerobic biological treatment will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the ratio of the biological oxygen demand-to-total organic carbon content, (b) the concentration of surfactants, and (c) the concentrations of toxic constituents and waste characteristics.

### 1.4.1 The Ratio of the Biological Oxygen Demand-to-Total Organic Carbon Content

Because organic constituents in the waste effectively serve as a feed supply for the microorganisms, it is necessary that a significant percentage be biodegradable. If they are not (i.e., a significant fraction of the organic constituents are refractory), it will be difficult for the microorganisms to successfully acclimate to the waste and achieve effective treatment. The percentage of biodegradable organics can be estimated by the ratio of the biological oxygen demand (BOD) to the total organic carbon (TOC) content. The biological oxygen demand is a measure of the amount of oxygen required for complete microbial oxidation of biodegradable organics. If the ratio of BOD to TOC in an untested waste is significantly lower than that in the tested waste, the system may not achieve the same performance and other, more applicable technologies may need to be considered for treatment of the untested waste.

### 1.4.2 Concentration of Surfactants

Surfactants can affect aerobic biological treatment performance by forming a film on organic constituents, thereby establishing a barrier to oxygen transfer and effective biodegradation. If the concentration of surfactants in an untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance and other, more applicable technologies may need to be considered for treatment of the untested waste.

### 1.4.3 Concentration of Toxic Constituents and Waste Characteristics

A number of constituents and waste characteristics have been identified as potentially toxic to microorganisms. Specific toxic concentrations have not been determined for most of these constituents and waste characteristics. The constituents and waste characteristics found to be potentially toxic to microorganisms include metals and oil and grease, as well as high concentrations of total dissolved solids, ammonia, and phenols. If the concentration of toxic constituents and waste characteristics in an untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance and other, more applicable technologies may need to be considered for treatment of the untested waste.

## 1.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of an aerobic biological treatment system, EPA examines the following parameters: (a) the amount of nutrients, (b) the concentration of dissolved oxygen, (c) the food-to-microorganism ratio, (d) the pH, (e) the aerobic biological treatment temperature, (f) the mean cell residence time, (g) the hydraulic loading rate, (h) the settling time, and (i) the degree of mixing.

### 1.5.1 Amount of Nutrients

Nutrient addition is important in controlling the growth of microorganisms because an insufficient amount of nutrients results in poor microbial growth with poor biodegradation of organic constituents. The principal inorganic nutrients used are nitrogen and phosphorus. In addition, trace amounts of potassium, calcium, sulfur, magnesium, iron, and manganese are also used for optimum microbial growth. The percent distribution of nitrogen and phosphorus added to microorganisms varies with the age of the organism and the particular environmental conditions. The total amount of nutrients required depends on the net mass of organisms produced.

EPA monitors the amount of nutrients added and their method of addition to the wastewater to ensure that a sufficient supply is provided to achieve an effective growth of microorganisms.

### 1.5.2 Concentration of Dissolved Oxygen

A sufficient concentration of dissolved oxygen (DO) is necessary to metabolize and degrade dissolved organic constituents. The DO concentration is controlled by adjusting the aeration rate. The aeration rate must be adequate to provide a sufficient DO concentration to satisfy the BOD requirements of the waste, as well as to provide adequate mixing to keep the microbial population in suspension (for activated sludge and aerated lagoon processes). EPA monitors the DO concentrations continuously, is possible, to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

### 1.5.3 Food-to-Microorganism Ratio

The food-to-microorganism (F/M) ratio applies only to activated sludge systems and is a measure of the amount of biomass available to metabolize the influent organic loading to the aeration unit. This ratio can be determined by dividing the influent BOD concentration by the concentration of active biomass, also referred to as the mixed liquor volatile suspended solids (MLVSS). The F/M ratio is controlled by adjusting the wastewater feed rate or the sludge recycle rate. If the F/M ratio is too high, too few microorganisms will be available to degrade the organics. EPA periodically analyzes the influent BOD and the aeration unit's MLVSS concentrations to ensure that the system is operating at the appropriate design condition.

### 1.5.4 pH

Generally, neutral or slightly alkaline pH favors microorganism growth. The optimum range for most microorganisms used in aerobic biological treatment systems is between 6 and 8. Treatment effectiveness is generally insensitive to changes within this range. However, pH values outside the range can lower treatment performance. EPA monitors the pH continuously, if possible, to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

### 1.5.5 Aerobic Biological Treatment Temperature

Microbial growth can occur under a wide range of temperatures, although the majority of the microbial species used in aerobic biological treatment processes are active between 20 and 35°C (69 to 95°F). The rate of biochemical reactions in cells increases with temperature up to a maximum above which the rate of activity declines as enzyme denaturation occurs and microorganisms either die off or become less active. EPA monitors the aerobic biological treatment temperature continuously, if possible, to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

### 1.5.6 Mean Cell Residence Time

In activated sludge and aerated lagoon systems, the mean cell residence time (MCRT) or sludge age is the length of time organisms are retained in the aeration unit before being drawn off as waste sludge. By controlling the MCRT, the growth phase of the microbial population can be controlled. The MCRT must be long enough to allow the organisms in the aeration unit to reproduce. The MCRT is determined by dividing the total active microbial mass in the aeration unit (MLVSS) by the total quantity of microbial mass withdrawn daily (wasted). EPA monitors the MCRT to ensure that an effective amount of microorganisms is present in the aeration unit.

### 1.5.7 Hydraulic Loading Rate

The hydraulic loading rate determines the length of time the organic constituents are in contact with the microorganisms and, hence, the extent of biodegradation that occurs. In trickling filters, the hydraulic loading rate also determines the shear velocities on the microbial layer. Excessively high hydraulic loading rates may wash away the microbial layer faster than it can grow back. However, the hydraulic loading rate must be high enough to keep the microbes moist and to remove dead or dying microbes that have lost their ability to cling to the filter media. For all aerobic biological treatment processes, the hydraulic loading rate is controlled by adjusting the wastewater feed rate. In addition, for RBCs, the hydraulic loading rate can be controlled by changing the disk speed or adjusting the submersion depth. EPA monitors the wastewater feed rates to ensure that the hydraulic loading provides sufficient time to achieve an effective biodegradation of organic constituents in the wastewater.

### 1.5.8 Settling Time

Adequate settling time must be provided to separate the biological solids from the mixed liquor. Activated sludge systems cannot function properly if the solids cannot be effectively separated and a portion returned to the aeration basin. EPA monitors the settling time to ensure effective solids removal.

### 1.5.9 Degree of Mixing

Mixing provides greater uniformity of the wastewater feed in the equalization basin to reduce variations that may cause process upsets of the microorganisms and diminish treatment efficiency. For activated sludge and aerated lagoon systems, sufficient aeration in the aeration unit provides mixing to ensure adequate contact between the microorganisms and the organic constituents in the wastewater. The quantifiable degree of mixing is a complex assessment that includes, among other things, the amount of energy supplied, the length of time the material is mixed, and the related turbulence effects of the specific size and shape of the mixing unit. This is beyond the scope of simple measurement. EPA, however, evaluates the degree of mixing qualitatively by considering whether mixing is provided and whether the type of mixing device is one that could be expected to achieve uniform mixing of the wastewater.

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# 2. BATCH DISTILLATION

## 2.1 Applicability

Batch distillation is one of several thermal treatment technologies applicable to the treatment of wastes containing organics that are volatile enough to be removed by the application of heat. This technology can be used to treat wastes having a high percentage of organics. Use of this technology results in an organic product stream that may be reusable directly or after further treatment and a bottom stream that is often incinerated.

## 2.2 Underlying Principles of Operation

As with other forms of distillation, the basic principle of operation for batch distillation is the separation of a liquid mixture into various components by a process of vaporization-condensation. The more volatile constituents, which are vaporized, are then condensed and either reused or further treated by liquid injection incineration; the less volatile constituents, which do not vaporize significantly, may also be reused, but are more often incinerated.

An integral part of the theory of batch distillation is the principle of vapor-liquid equilibrium. When a liquid mixture of two or more components is heated, the vapor phase present above the liquid phase becomes more concentrated in the more volatile constituents (i.e., those having higher vapor pressures). The vapor phase above the liquid phase is then cooled to yield a condensate that is also more concentrated in the more volatile components. The remaining liquid phase is richer in the less volatile components. The degree of separation of components depends on the relative differences in the vapor pressures of the constituents; the larger the difference in the vapor pressures, the more easily the separation can be accomplished.

If the difference between the vapor pressures is extremely large, a single equilibrium stage of vaporization and condensation may achieve a significant separation of the constituents. (Refer to the fractionation technology, Section 12, for a discussion of equilibrium stages.) Typically, batch distillation units contain only one equilibrium stage and are thus limited in the degree of separation by the relative volatilities of the constituents. The greater the difference in component volatilities, the more likely it is that batch distillation will be effective.

The vapor-liquid equilibrium of the waste components can be expressed as relative volatility, which is the ratio of the vapor-to-liquid concentrations of a constituent divided by the ratio of the vapor-to-liquid concentrations of another constituent. The relative volatility is a direct indicator of the ease of separation. If the numerical value is 1, then separation using distillation is impossible because the constituents have the same concentrations in the vapor and liquid phases. When the relative volatility is 1, the liquid mixture is called an azeotrope. Separation becomes easier as the value of the relative volatility becomes increasingly different from unity. As more of the volatiles are removed, the temperature must be continually raised to vaporize the remaining waste.

In batch distillation, pressurized steam is usually the source of the heat. The process usually takes place at temperatures lower than approximately 340°F (corresponding to steam at a pressure of 120 psig) when atmospheric pressure exists in the distillation unit. For batch distillation units operating under a vacuum, the constituents of concern that can be volatilized could have boiling points up to 450°F at atmospheric pressure.

## 2.3 Description of Batch Distillation Process

A batch distillation unit consists of a steam-jacketed vessel, a condenser, and a product receiver. Figure 2-1 is a schematic showing the major components of a batch distillation unit. The steam jacket provides the heat required to vaporize the volatile constituents in the liquid fraction of the waste. The rising vapor is collected in the condenser, cooled, and condensed. The liquid product stream is then routed to the product receiver.

It is important to note that this technology treats wastes by vaporizing constituents, not destroying them. Accordingly, an integral part of this technology is a condensation system to collect the organics, as well as an air emission control system to collect those organics that are not condensed. The cooling load of the condenser is calculated in the design to ensure that the product recovery rate is maximized and emissions from condenser venting are minimized.

The "bottoms," which are the least volatile constituents of the waste, are withdrawn from the bottom of the batch still. Because batch distillation is used to remove the volatile organics from wastes, the bottoms are reduced in volatile organic content. However, the bottoms generally require additional treatment, such as incineration for residual, less volatile organics, prior to disposal.

## 2.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether batch distillation will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the thermal conductivity of the waste, (b) the component boiling points, and (c) the concentration of volatile components.

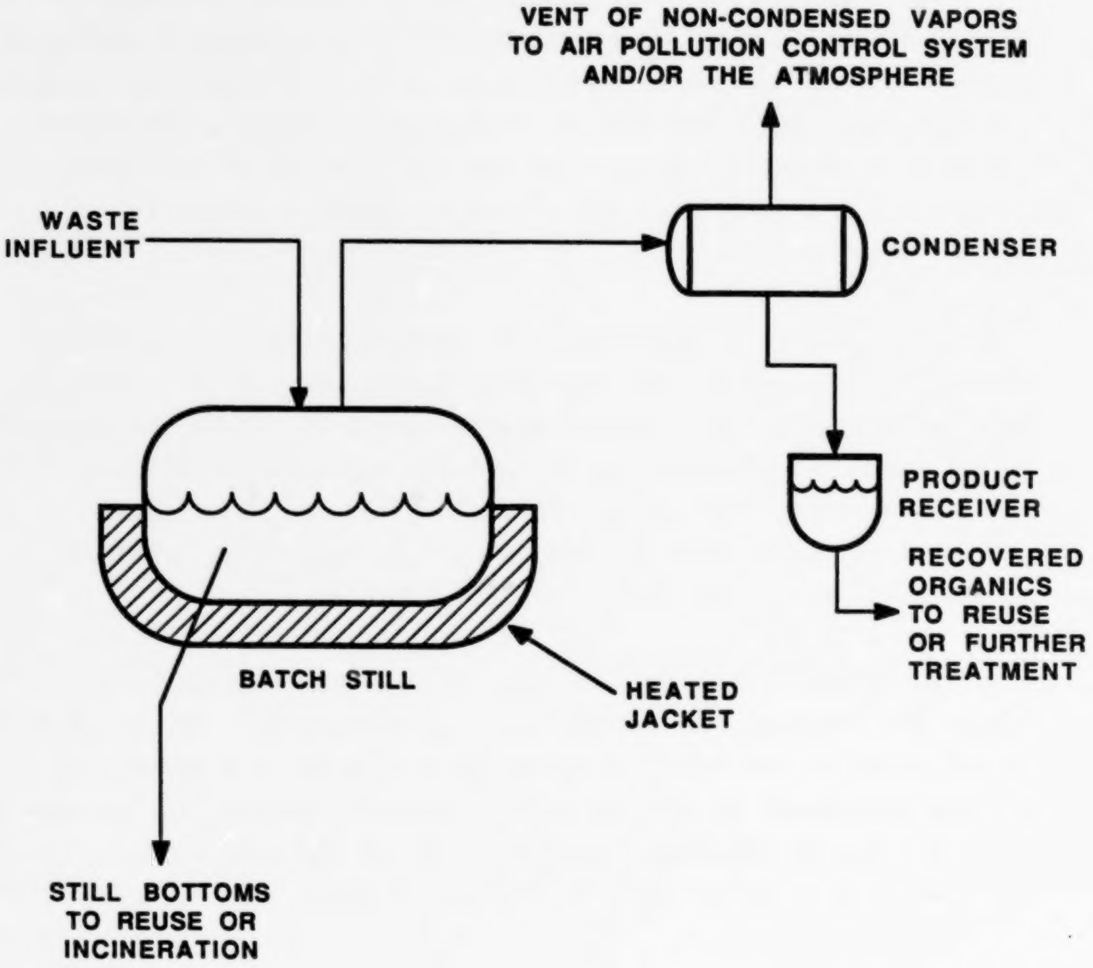
VENT OF NON-CONDENSED VAPORS TO AIR POLLUTION CONTROL SYSTEM AND/OR THE ATMOSPHERE
WASTE INFLUENT
CONDENSER
PRODUCT RECEIVER
RECOVERED ORGANICS TO REUSE OR FURTHER TREATMENT
BATCH STILL
HEATED JACKET
STILL BOTTOMS TO REUSE OR INCINERATION

Figure 2-1. Batch Distillation System.

### 2.4.1 Thermal Conductivity of the Waste

A major factor determining whether a particular constituent will volatilize is the transfer of heat through the waste. For batch distillation, heat transfer is accomplished principally by conduction when the source of heat is indirect steam and by both convection and conduction when the heat source is direct steam injection.

EPA examined both methods of heat transfer and believes that conduction would be the primary cause of heat transfer differences between wastes. Heat flow by conduction is proportional to the temperature gradient across the material. The proportionality constant, referred to as the thermal conductivity, is a property of the material to be distilled. With regard to convection, EPA believes that the amount of heat transferred by convection will generally be more a function of the system design than of the waste itself.

Thermal conductivity measurements, as part of a treatability comparison for two different wastes to be treated by a single batch distillation unit, are most meaningful when applied to wastes that are homogeneous (i.e., uniform throughout). As wastes exhibit greater degrees of nonhomogeneity, thermal conductivity becomes less accurate in predicting treatability because the measurement essentially reflects heat flow through regions having the greatest conductivity (i.e., the path of least resistance) and not heat flow through all parts of the waste. Nevertheless, EPA believes that thermal conductivity may provide the best measure of performance transfer. If the thermal conductivity of an untested waste is significantly lower than that of the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 2.4.2 Component Boiling Points

As noted earlier, the greater the ratio of volatility of the waste constituents, the more easily the separation of these constituents can proceed. This ratio is called relative volatility. EPA recognizes, however, that relative volatilities cannot be measured or calculated directly for the types of wastes generally treated by batch distillation.

This is because the wastes usually consist of a myriad of components, all with different vapor pressure-versus-temperature relationships. However, because the volatility of components is usually inversely proportional to their boiling points (i.e., the higher the boiling point, the lower the volatility), EPA uses the boiling point of waste components as a surrogate waste characteristic for relative volatility. If the differences in boiling points between the more volatile and less volatile constituents are significantly lower in the untested waste than in the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 2.4.3 Concentration of Volatile Components

The concentration of volatile components is a measure of the maximum fraction of the waste that can be expected to volatilize in the batch still. A relatively low concentration of volatile components implies that most of the waste may become bottoms (i.e., is nonvolatile). If the concentration of volatile components in the untested waste is significantly lower than that in the tested waste, the system may not achieve the same performance. Higher temperatures may be required to volatilize less volatile components and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 2.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a batch distillation system, EPA examines the following parameters: (a) the distillation temperature and pressure and (b) the residence time.

### 2.5.1 Distillation Temperature and Pressure

Temperature provides an indirect measure of the energy available (i.e., Btu/hr) to vaporize the waste constituents. As the design temperature increases, more constituents with lower volatilities will be removed from the waste.

Pressure is integrally related to the boiling point of the waste and the subsequent vaporization of the organic constituents. As the pressure is lowered below atmospheric (i.e., as vacuum is increased), the boiling point of the waste will also be lowered, thereby requiring less heat input to volatilize waste constituents. EPA monitors the distillation temperature as well as the pressure (if pressures other than atmospheric are used) to ensure that the system is operating at the appropriate design conditions and to diagnose operational problems.

### 2.5.2 Residence Time

The residence time determines the necessary energy input into the system as well as the degree of volatilization of organic constituents. It is dependent on the distillation temperature and the thermal conductivity of the waste. EPA observes the residence time to ensure that sufficient time is provided to effectively volatilize organic constituents from the waste.

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# 3. CARBON ADSORPTION

## 3.1 Applicability

Carbon adsorption is a treatment technology used to treat wastewaters containing dissolved organics at concentrations less than 1,000 mg/l and, to a lesser extent, dissolved metal and other inorganic contaminants. The most effective metals removal is achieved with metal complexes.

The two most common carbon adsorption processes are the granular activated carbon (GAC), which is used in packed beds, and the powdered activated carbon (PAC), which is added loosely to wastewater. This section discusses the GAC process; the PAC process is discussed in Section 9 of this report, Aerobic Biological Treatment.

## 3.2 Underlying Principles of Operation

The basic principle of operation for carbon adsorption is the mass transfer and adsorption of a molecule from a liquid or gas onto a solid surface. Activated carbon is manufactured in such a way as to produce extremely porous carbon particles whose internal surface area is very large (500 to 1,400 square meters per gram of carbon). This porous structure attracts and holds (adsorbs) organic molecules as well as certain metal and inorganic molecules.

Adsorption occurs because: (1) the contaminant has a low solubility in the waste, (2) the contaminant has a greater affinity for the carbon than for the waste, or (3) a combination of the two. The amount of contaminants that can be adsorbed by activated carbon ranges from 0.10 to 0.15 gram per gram of carbon.

## 3.3 Description of Carbon Adsorption Process

In GAC systems, the carbon is packed in a column and the wastewater is passed through the carbon bed(s). The flow can be either down or up through the vertical column(s). Figure 3-1 shows two carbon adsorption systems. In the carbon adsorption process, the wastewater is passed through a stationary bed of carbon. The contaminants in the wastewater are adsorbed most rapidly and effectively by the upper layers of carbon during the initial stages of operation. These upper layers are in contact with the wastewater at its highest concentrations of contaminants. The small amounts of the contaminants that are not adsorbed in the first few layers of the activated carbon bed are removed from solution in the lower or downstream portion of the bed. Initially, none of the contaminants escapes from the carbon bed.

As the wastewater flows down the column (or the location in the column where the majority of adsorption is occurring), and the adsorption capacity is reached in the top layers, the adsorption zone moves down the column. As the adsorption zone approaches the end of the carbon bed, the concentration in the effluent rapidly approaches the influent concentration. This point in the process is referred to as breakthrough. A breakthrough curve (Figure 3-2) shows the plot of the ratio of effluent to influent concentrations versus time of process operation. At breakthrough, the adsorptive capacity of the carbon bed is exhausted, and little additional removal of contaminants occurs. Treated wastewater is then either treated further in another carbon adsorption column, if necessary, or disposed of.

Once the carbon bed is spent and can no longer remove contaminants from the waste, it is taken off-line. The activated carbon is then either regenerated by thermal or chemical methods for further use or treated by incineration and disposed of. If carbon adsorption is used to

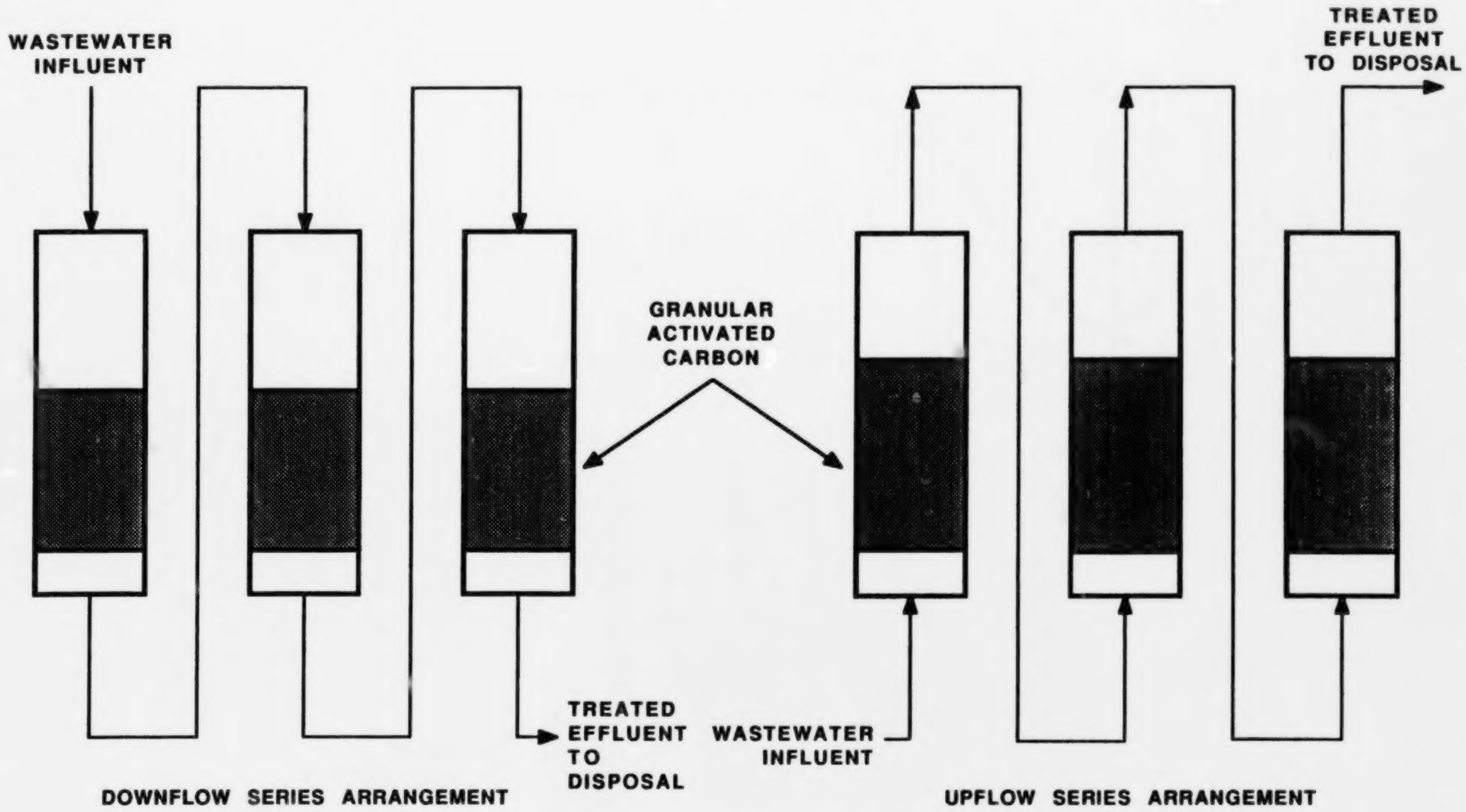
WASTEWATER INFLUENT
TREATED EFFLUENT TO DISPOSAL
DOWNFLOW SERIES ARRANGEMENT
GRANULAR ACTIVATED CARBON
WASTEWATER INFLUENT
TREATED EFFLUENT TO DISPOSAL
UPFLOW SERIES ARRANGEMENT

Figure 3-1. Carbon Adsorption Systems.

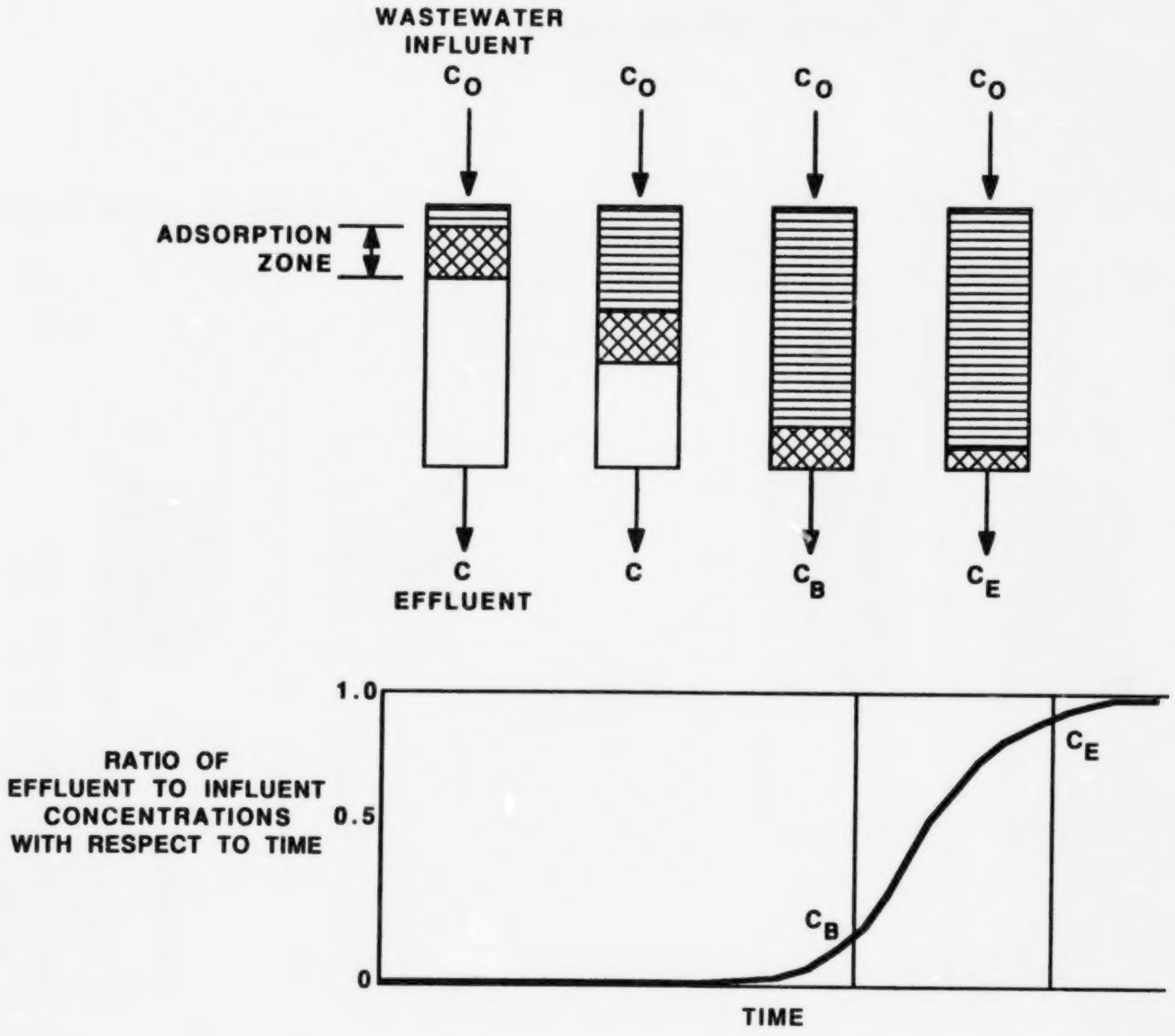
WASTEWATER INFLUENT
$C_O$
$C_O$
$C_O$
$C_O$
ADSORPTION ZONE
C
EFFLUENT
C
$C_B$
$C_E$
RATIO OF EFFLUENT TO INFLUENT CONCENTRATIONS WITH RESPECT TO TIME
1.0
0.5
0
$C_B$
$C_E$
TIME

Figure 3-2. Plot of Breakthrough Curve.

treat very toxic or hazardous materials, the spent carbon generally is incinerated and disposed of directly.

Regeneration is accomplished thermally by heating the carbon to a temperature (between 1,500 and 1,700°F) at which most of the adsorbed contaminants are volatilized and destroyed but which is not high enough to burn the surface of the carbon. About 4 to 9 percent of the carbon is lost in this process. Steam can also be used to regenerate carbon by volatilizing adsorbed organics for subsequent condensation, recovery and reuse or for treatment and disposal. Chemical regeneration involves the use of an acid, alkali, or organic solvent to redissolve contaminants for subsequent recovery and reuse or for further treatment and disposal. There is a loss of performance with each regeneration of spent carbon because metals (such as calcium, magnesium, and iron), plug small pores in the carbon and prevent some organic contaminants from being desorbed at the thermal regeneration temperature. In each thermal regeneration process, some carbon becomes spent, requiring treatment and disposal. As a result, makeup carbon has to be added to the regenerated carbon being placed back in service.

The number of times that the carbon can be regenerated is determined by the extent of its physical erosion and the loss of its adsorptive capacity. Isotherm tests can be performed on the regenerated carbon to determine adsorptive capacity; such tests can thus aid in predicting the number of times the carbon can be regenerated.

## 3.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether carbon adsorption will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the type and concentration and type of adsorbable contaminants and (b) the concentrations of suspended solids and oil and grease.

### 3.4.1 Type and Concentration and Type of Adsorbable Contaminants

The concentration of adsorbable contaminants is a measure of the fraction of the wastewater constituents that can be expected to be adsorbed by a carbon adsorption column. Concentrations of organics in the wastewater greater than about 1,000 mg/l results in excessive activated carbon consumption requiring frequent regeneration.

While all organics can be adsorbed to some degree, activated carbon has a greater affinity for aromatic rather than for aliphatic compounds and for nonpolar rather than for polar compounds. If the type and concentration of adsorbable contaminants in an untested waste are significantly less adsorbable and higher, respectively, than in the tested waste, the system may not achieve the same performance.

### 3.4.2 Concentrations of Suspended Solids and Oil and Grease

Suspended solids and oil and grease can reduce the effectiveness of carbon adsorption by clogging and coating the pores, as well as by competing for adsorption sites, thereby interfering with the treatment of contaminants of concern.

## 3.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a carbon adsorption system, EPA examines the following parameters: (a) the type and pore size of the carbon particles, (b) the adsorption temperature, (c) the pH, and (d) the hydraulic loading rate.

### 3.5.1 Type and Pore Size of Carbon Particles

Activated carbon is made from a variety of substances (e.g., coal, wood), ground to many different sizes, and manufactured with a number of different pore sizes. The pore size determines the surface area available for adsorption and, hence, the carbon's adsorptive capacity. The type and pore size of carbon particles exhibit different adsorptive capacities for different contaminants. Another property that is important in assessing the effectiveness of carbon particles is the iodine number; this value is an indicator of the adsorptive capacity for low molecular weight organics. Laboratory bench testing is used to determine the most effective type and pore size of carbon particles for treating particular wastewaters. EPA examines the type and pore size of the carbon particles used to ensure that effective adsorption is achieved.

### 3.5.2 Adsorption Temperature

As the temperature increases, the solubility of the contaminants generally increases as well, which results in less effective adsorption. EPA monitors the temperature continuously, if possible, to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

### 3.5.3 pH

The pH impacts both the solubility of the various contaminants and the potential for chemical bonding to occur. EPA monitors the pH continuously, if possible, to ensure that the system is operating at the appropriate design conditions to diagnose operational problems.

### 3.5.4 Hydraulic Loading Rate

The amount of time that the waste contaminants are in contact with the carbon particles (i.e., residence time) impacts the extent to which adsorption occurs. Higher residence times generally improve adsorption performance but require longer carbon beds to maintain the same overall through-put. Typical residence times for GAC adsorption systems range from 30 to 100 minutes. For a given size carbon bed, the residence time can be determined by the hydraulic loading rate. Typical hydraulic loading rates for downflow adsorption systems range from 0.5 to 8.0 gal/min-ft$^2$, while upflow systems typically operate around 15 gal/min-ft$^2$. EPA monitors the hydraulic loading rate to ensure that sufficient time is provided to effectively adsorb contaminants.

## 3.6 References

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# 4. CRITICAL FLUID EXTRACTION

## 4.1 Applicability

Critical fluid extraction is a treatment technology applicable to wastes containing a variety of organics that are soluble in pressurized fluids such as carbon dioxide, propane, butane, or pentane. Compounds that have been extracted from wastes by this process include aliphatic hydrocarbons, alkenes, simple aromatic solvents such as benzene and toluene, polynuclear aromatics, and phenols. In theory, this process should also be applicable to a variety of other organic waste constituents. Critical fluid extraction has been demonstrated for treatment of API separator sludges and other hydrocarbon-bearing wastes generated by the petroleum and petrochemicals industries. It may also be applicable to wastes of similar composition generated by other industries such as the organic chemicals industry.

## 4.2 Underlying Principles of Operation

The basic principle of operation for critical fluid extraction the enhanced solubilities of various organic compounds in hydrocarbons and other solvents in the near critical state (i.e., high pressure) aids in their removal from a waste. The solvents used are compounds that are usually gases at ambient conditions. The volatile organic solvent is pressurized, which converts it from a gas to a liquid. As a liquid, it leaches (dissolves) the organic constituents out of the complex waste with which it is mixed.

## 4.3 Description of Critical Fluid Extraction Process

A critical fluid extraction process consists of a blending tank, one or more extraction vessels, one or more decantors, one or more filters, and an evaporation unit. Oil refinery sludges or other organic wastes are first blended together in a blending tank and mixed well to yield a homogeneous, pumpable mixture. This mixture is then pumped to an extraction vessel filled with a liquified gas such as carbon dioxide, propane, butane, or pentane and is mixed under pressure to extract (dissolve) hydrocarbon components from the waste into the liquified gas solvent. After the hydrocarbon components of the waste dissolve in the pressurized liquid, the resulting solution is gravity-separated in a decanter into a wastewater (or waste solids) stream and a solvent-rich stream. The wastewater stream, containing inorganic solids, is sometimes filtered under pressure to remove the insoluble components. The solvent-rich stream is fed to a pressurized evaporation unit. The solvent (carbon dioxide, propane, butane, or pentane) is evaporated by dropping the pressure and is subsequently recovered, repressurized, and recondensed for reuse. The residue from the evaporation, consisting of a liquid hydrocarbon mixture, is then returned to the refinery or other process plant for reprocessing and/or reuse, blended with fuels for heat recovery, or incinerated.

The inorganic residuals (or waste solids) filtered from the waste/solvent mixture are either land disposed (if they contain nontreatable levels of hazardous constituents such as certain metals (e.g., chromium, lead)) or further treated by processes such as stabilization (and/or incineration if waste solids contain treatable organic levels) prior to land disposal.

## 4.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether critical fluid extraction will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the concentration of extractable hydrocarbons, (b) the alkalinity of the waste, and (c) the solubility of the waste constituents of concern in the solvent.

### 4.4.1 Concentration of Extractable Hydrocarbons

The process is designed to extract hydrocarbon components from mixed oily and organic waste liquids and sludges. For this process to be economically applied, the waste should contain at least a few percent by weight of extractable hydrocarbons. The process has been demonstrated on wastes containing from 5 to 34 percent hydrocarbons. For lower concentrations, batch distillation or conventional solvent extraction may be more economical. Also, critical fluid extraction is not economical for wastes containing high concentrations of extractable hydrocarbons (higher than 95 percent). These wastes are more amenable to fractionation treatment. The concentration of extractable hydrocarbons in the waste feed is a measure of the maximum fraction of the waste that can be expected to be extracted in the critical fluid extraction process. A relatively low concentration of extractable hydrocarbons implies that most of the waste may become wastewater or waste solids (i.e., is nonextractable). Total extractable hydrocarbon content can be estimated by measurement of the total organic carbon (TOC) content. If the TOC of an untested waste is significantly lower than that of the tested waste, the system may not achieve the same performance. More rigorous extraction conditions such as higher temperatures and pressures, additional mixing, and longer settling times may be required to extract less extractable components and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 4.4.2 Alkalinity of the Waste

When carbon dioxide is used as the extraction fluid, high alkalinity will interfere with the process because carbon dioxide will react to form carbonates and bicarbonates. This will result in excessive carbon dioxide consumption. For wastes having high alkalinity levels, an extraction fluid other than carbon dioxide should be used. The same problem does not arise if a hydrocarbon fluid (propane, butane, or pentane) is used. If carbon dioxide was the extraction fluid used on a tested waste and the alkalinity of the untested waste is significantly higher than that of the tested waste, the system may not achieve the same performance. Use of another extraction fluid may be required to achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 4.4.3 Solubility of the Waste Constituents of Concern in the Solvent

The constituents in the waste feed that are to be extracted determine the solvent best suited for the extraction process. If the solubility of the waste constituents of concern in the solvent in the untested waste is significantly lower than that in the tested waste, the system may not achieve the same performance. Use of another solvent may be required to increase the solubility of the waste constituents of concern and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 4.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a critical fluid extraction system, EPA examines the following parameters: (a) the extraction pressure, (b) the degree of initial waste mixing, (c) the degree of mixing during extraction, (d) the extraction temperature, (e) the residence time, and (f) the settling time.

### 4.5.1 Extraction Pressure

Critical fluid extraction systems operate at pressures at which the critical fluids will be liquids at ambient temperatures. Pressure is normally monitored by means of gauges and recorders attached to the extraction vessel. EPA monitors the extraction pressure continuously, if possible, to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

### 4.5.2 Degree of Initial Waste Mixing

The waste must be premixed before introduction into the extraction system to ensure a uniform, pumpable blend of material. The waste is normally mixed in tanks or other vessels. Any well-designed and well-operated system should have such waste-blending equipment. The quantifiable degree of mixing is a complex assessment that includes, among other things, the amount of energy supplied, the length of time the material is mixed, and the related turbulence effects of the specific size and shape of the tank or vessel. This is beyond the scope of simple measurement. EPA, however, evaluates the degree of mixing qualitatively by considering whether mixing is provided and whether the type of mixing device is one that could be expected to achieve uniform mixing of the waste.

### 4.5.3 Degree of Mixing During Extraction

During the fluid extraction, the solvent and waste need to be mixed to ensure maximum contact and, hence, efficiency of extraction. Any well-designed system should include a pressurized extraction vessel that is equipped with an operable mixing system. EPA evaluates this mixing in the same manner as that previously described for initial waste mixing.

### 4.5.4 Extraction Temperature

The process is normally operated at ambient temperature, although it is possible to use higher temperatures when necessary. In all cases, temperatures used must be below the critical temperature* of the solvent used to ensure that the solvent is present in the extraction vessel in the liquid phase (so that maximum contact with the waste can be achieved). EPA monitors the extraction temperature continuously, if possible, to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

### 4.5.5 Residence Time

The residence time in the extraction vessel impacts the extent of extraction of organic contaminants from the waste. It is dependent on the solubility of the waste constituents of concern in the solvent. EPA monitors the waste feed rate to ensure that sufficient residence time is provided to effectively extract the organic contaminants from the waste.

### 4.5.6 Settling Time

Adequate settling time must be provided to make sure that separation of the phases has been effectively completed. EPA monitors the settling time to ensure effective phase separation.

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* The critical temperature of a substance is that temperature above which the substance cannot be liquified, no matter how high the operating pressures.

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# 5. FRACTIONATION

## 5.1 Applicability

Fractionation is a form of distillation applicable to wastes containing organics that are volatile enough to be separated from other components by the application of heat. It differs from other forms of distillation, such as batch distillation, steam stripping, and thin film evaporation, in that it is designed to achieve the highest degree of distillate purity of the separated components. Fractionation can be operated to produce multiple product streams for recovery of more than one organic constituent from a waste while generating minimal amounts of residue to be land disposed. In general, this technology is used where recovery of multiple constituents is desired and where the waste contains minimal amounts of suspended solids.

## 5.2 Underlying Principles of Operation

As with other forms of distillation, the basic principle of operation for fractionation is the volatilization of the more volatile constituents from the less volatile constituents through the application of heat. The constituents that are volatilized are then condensed and typically reused. Constituents that are not volatilized may also be reused or incinerated as applicable.

An integral part of the theory of fractionation is the principle of vapor-liquid equilibrium. When a liquid mixture of two or more components is heated, the vapor phase present above the liquid phase becomes more concentrated in the more volatile constituents (those having the higher vapor pressures). The vapor phase above the liquid phase is then cooled to yield a condensate that is also more concentrated in the more volatile components. The remaining liquid phase is richer in the less volatile components. The degree of separation of components depends on the relative differences in the vapor pressures of the constituents; the larger the difference in the vapor pressures, the more easily the separation can be accomplished.

If the difference between the vapor pressures is extremely large, a single separation cycle or a single equilibrium stage of vaporization and condensation may achieve a significant separation of the constituents. (Typically, batch distillation or thin film evaporation would be used in such a case). If the difference between the vapor pressures is small, then multiple equilibrium stages are needed to achieve effective separation. In practice, the multiple equilibrium stages are obtained by stacking trays or placing packing into a column. Essentially, each tray represents one equilibrium stage. In a packed fractionation column, the individual equilibrium stages are not discernible, but the number of equivalent trays can be calculated from mathematical relationships using the height of the packing. The vapor phase from a tray rises to the tray above it, where it condenses; the liquid phase falls to the tray below it, where it is again heated and separated. Fractionation processes use multiple equilibrium stages, with the initial waste feed entering at a point between the first and last equilibrium stages.

The stages at and below the point of entry are called the stripping section. These stages sequentially "strip" the volatile components from the liquid feed (i.e., reduce the quantities of more volatile constituents). The stages located above the point of feed are called the rectification section. These stages allow the vapor rising from the stripping section to become further enriched in the more volatile components. The vapor leaving the top of the fractionating column is condensed, and a portion of this condensed liquid is returned to the uppermost stage to aid in rectification. This step of returning a portion of the condensed liquid to the column is called reflux. The remaining condensed liquid is collected in a product receiver and reused.

The vapor-liquid equilibrium of the waste components can be expressed as relative volatility, which is the ratio of the vapor-to-liquid concentrations of a constituent divided by the vapor-to-liquid concentrations of another constituent. The relative volatility is a direct indicator of the ease of separation. If the numerical value is 1, then separation is impossible because the constituents have the same concentrations in the vapor and liquid phases. When the relative volatility is 1, the liquid mixture is called an azeotrope. Separation becomes easier as the value of the relative volatility becomes increasingly different from unity.

## 5.3 Description of Fractionation Process

A fractionation unit consists of a reboiler, a column containing stripping and rectification sections, a condenser, and a reflux system. Figure 5-1 is a schematic showing the major components of a fractionation unit. The reboiler is a device that provides the heat required to vaporize the liquid fraction of the waste. It supplies enough heat to maintain the liquid in the column at its boiling point. The stripping and rectifying sections are composed of a set of trays in a vertical column. The discrete trays may be replaced by loose packing consisting of plastic, metal, or ceramic geometric shapes that provide surface area for the continuous boiling/condensing that takes place in the column. In the stripping section, vapor rising from the boiler is contacted with the downflowing liquid feed. Through this contact, the constituents with lower boiling points (i.e., those that are more volatile) are concentrated in the vapor. In the rectification section, the vapor rising above the feed tray is contacted with downflowing condensed liquid product (reflux). Through this contact, further enrichment of the vapor in the constituents with lower boiling points (i.e., the more volatile constituents) is achieved. The rising vapor is collected at the top of the column and condensed in a condenser. The liquid product stream,

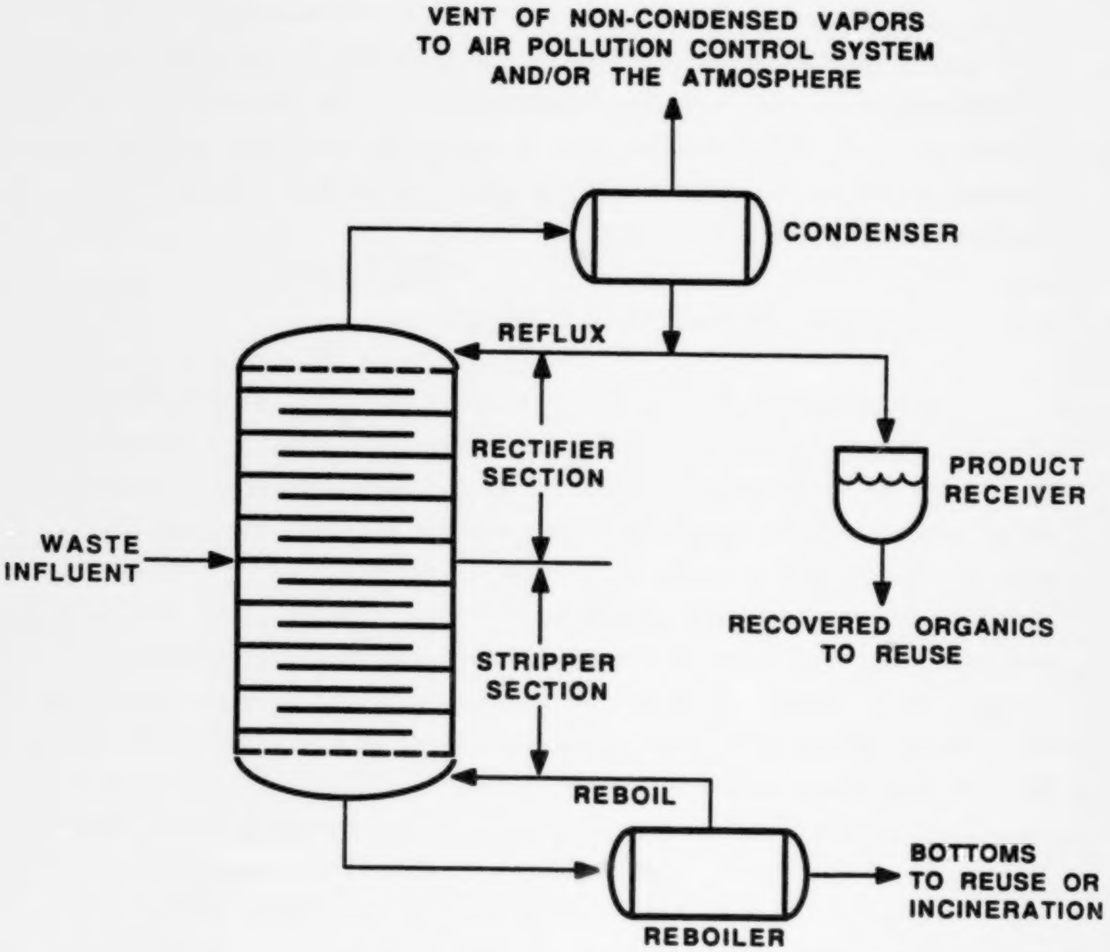
VENT OF NON-CONDENSED VAPORS
TO AIR POLLUTION CONTROL SYSTEM
AND/OR THE ATMOSPHERE
CONDENSER
REFLUX
RECTIFIER
SECTION
PRODUCT
RECEIVER
WASTE
INFLUENT
RECOVERED ORGANICS
TO REUSE
STRIPPER
SECTION
REBOIL
BOTTOMS
TO REUSE OR
INCINERATION
REBOILER

Figure 5-1. Fractionation System.

except for the portion returned to the column as reflux, is then routed to a product receiver. The "bottoms," which are the least volatile components (i.e., those with the highest boiling points), are continuously withdrawn from the reboiler.

Because the liquid composition varies slightly from one equilibrium stage to the next, it is also possible to withdraw streams of differing quality (sometimes called "fractions") from different locations throughout the column. This is typically done in refining petroleum, resulting in different grades or "cuts" of petroleum products.

## 5.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether fractionation will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the component boiling points, (b) the concentration of suspended solids, (c) the concentration of volatile components, (d) the surface tension, and (e) the concentration of oil and grease.

### 5.4.1 Component Boiling Points

As noted earlier, the greater the ratio of volatility of the waste constituents, the more easily the separation of these constituents can proceed. This ratio is called relative volatility. EPA recognizes, however, that relative volatilities cannot be measured or calculated directly for the complex types of wastes generally treated by fractionation. This is because the wastes usually consist of a myriad of components, all with different vapor pressure-versus-temperature relationships. Determining relative volatilities is further complicated by the fact that the relative volatility changes as the temperature conditions change throughout the fractionation column (the column is cooler at the top than at the bottom). However, because the volatility of components is usually inversely proportional to their boiling points (i.e., the higher the boiling point, the lower the volatility), EPA uses the boiling point of waste components as a surrogate waste characteristic for relative volatility. If the differences in boiling points between the more volatile and less volatile constituents are lower in the untested waste than in the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 5.4.2 Concentration of Suspended Solids

Wastes containing large amounts of suspended solids, organic or inorganic, may clog column internals and coat heat transfer surfaces, thereby inhibiting mass transfer of constituents between the vapor and liquid phases. If the concentration of suspended solids in the untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance. Filtration may be required prior to fractionation to reduce the concentration of suspended solids and achieve the same treatment performance, or other, more applicable technologies may need to be considered for treatment of the untested waste.

### 5.4.3 Concentration of Volatile Components

The concentration of volatile components is a measure of the maximum fraction of the waste that can be expected to volatilize in the fractionation column. A relatively low concentration of volatile components implies that most of the waste may become bottoms (i.e., is nonvolatile). If the concentration of volatile components in the untested waste is significantly lower than that in the tested waste, the system may not achieve the same performance. Higher temperatures, lower pressures, and/or an increase in the number of separation stages may be required to volatilize less volatile components and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 5.4.4 Surface Tension

The surface tension of the waste is a measure of the tendency of the waste to foam. The higher the surface tension of the liquid, the higher its tendency to foam. The likelihood of foaming requires special column design or the incorporation of defoaming compounds. Packed columns are usually less susceptible to foaming than tray columns. If the surface tension of the untested waste is significantly higher than that of the tested waste, the system may not achieve the same performance. Defoaming compounds and/or the use of a packed column may be required to reduce foaming and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 5.4.5 Concentration of Oil and Grease

High concentrations of oil and grease may clog fractionation equipment. Consequently, special designs may be required to accommodate oil and grease. If the concentration of oil and grease in the untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 5.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a fractionation system, EPA examines the following parameters: (a) the number of separation stages, (b) the liquid and vapor flow rates, (c) the fractionation temperature and pressure, (d) the differential pressure, and (e) the internal column design.

### 5.5.1 Number of Separation Stages

The number of theoretical stages in the fractionation column required to achieve the desired separation of more volatile components from less volatile components is calculated from vapor-liquid equilibrium data, which are determined empirically. Using the theoretical number of stages, the actual number of stages can then be determined through the use of empirical tray efficiency data typically supplied by an equipment manufacturer. EPA examines the actual number of stages in the fractionation column to ensure that the system is designed to achieve an effective degree of separation of more volatile components from less volatile components.

### 5.5.2 Liquid and Vapor Flow Rates

The vapor-liquid equilibrium data are also used to determine the liquid and vapor flow rates that provide sufficient contact between the liquid and vapor streams. These rates are, in turn, affected by the column diameter. EPA monitors the liquid and vapor flow rates to ensure that sufficient contact time between the liquid and vapor streams is provided to effectively separate the more volatile components from less volatile components.

### 5.5.3 Fractionation Temperature and Pressure

These parameters are integrally related to the vapor-liquid equilibrium conditions. The temperature at any point in the column is an indicator of the constituent concentrations at that point, thus revealing whether the separation of components is taking place as expected. Overall column pressure influences the boiling point of the liquid at any location in the column. For example, through application of a partial vacuum to the column, the temperatures required to achieve the desired separation can be reduced because liquids volatilize at lower temperatures at reduced pressures. EPA monitors the temperature and pressure in a fractionation column continuously, if possible, to ensure that the system is operating at the appropriate design conditions and to diagnose operational problems.

### 5.5.4 Differential Pressure

Measuring the differential pressure between the top and bottom of the column indicates whether the flow rate of either the liquid or the vapor phase is excessive. For instance, a high pressure drop across the column may indicate a condition of "flooding," in which the liquid phase cannot flow down through the column as fast as feed is entering, causing backing up or "flooding" to occur. EPA monitors the pressure drop across the fractionation column continuously, if possible, to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

### 5.5.5 Internal Column Design

Column internals are designed to accommodate the physical and chemical properties of the waste to be fractionated. Two types of internals may be used in fractionation: trays and packing. Tray types include bubble cap, sieve, valve, and turbo-grid. Trays have several advantages over packing. They are less susceptible to blockage by solids, they have a lower capital cost for large-diameter columns (greater than approximately 3 feet), and they accommodate a wider range of liquid and vapor flow rates. Compared to trays, packing has the advantages of having a lower pressure drop per theoretical stage, being more resistant to corrosive materials, having a lower capital cost for small-diameter columns (less than approximately 3 feet), and being less susceptible to foaming because of a more uniform flow distribution (i.e., lower local variations in flow rates). EPA examines the internal column design of a fractionation column to ensure that the system is designed to handle potential operational problems (e.g., corrosion, foaming, channeling, etc.).

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# 6. FUEL SUBSTITUTION

Fuel substitution involves using hazardous waste as a fuel in industrial furnaces or in boilers for generation of steam. The hazardous waste may be blended with other nonhazardous wastes (e.g., municipal sludge) and/or fossil fuels.

## 6.1 Applicability

Fuel substitution has been used with industrial waste solvents, refinery wastes, synthetic fibers/petrochemical wastes, and waste oils. It can also be used when combusting other waste types produced during the manufacture of pharmaceuticals, pulp and paper, and pesticides. These wastes can be handled in a solid, liquid, or gaseous form.

The most common types of units in which waste fuels are burned are industrial furnaces and industrial boilers. Industrial furnaces include a variety of industrial processes that produce heat and/or products by burning fuels. They include blast furnaces, smelters, and coke ovens. Industrial boilers are units wherein fuel is used to produce steam for process and plant use. Industrial boilers typically use coal, oil, or gas as the primary fuel source.

The parameters that affect the applicability of fuel substitution are the:

- Halogen content of the waste;
- Inorganic solids content (ash content) of the waste, particularly heavy metals;
- Heating value of the waste;
- Viscosity of the waste (for liquids);

- Filterable solids concentration (for liquids); and
- Sulfur content.

### 6.1.1 Halogen Content of the Waste

If halogenated organics are burned, halogenated acids and free halogen are among the products of combustion. These released corrosive gases may require subsequent treatment prior to venting to the atmosphere. Also, halogens and halogenated acids formed during combustion are likely to severely corrode boiler tubes and other process equipment. To minimize such problems, halogenated wastes are blended into fuels only at very low concentrations. High chlorine content can also lead to the incidental production (at very low concentrations) of other hazardous compounds such as polychlorinated biphenyls (PCBs), chlorinated *dibenzo-p-dioxins* (CDDs), chlorinated dibenzofurans (CDFs), and chlorinated phenols.

### 6.1.2 Inorganic Solids Content of the Waste

High inorganic solids content (i.e., ash content) of wastes may cause two problems: (1) scaling in the boiler and (2) particulate air emissions. Scaling results from deposition of inorganic solids on the walls of the boiler. Particulate emissions are produced by noncombustible inorganic constituents that flow out of the boiler with the gaseous combustion products. Because of these problems, wastes with significant concentrations of inorganic materials are not usually handled in boilers unless they have an air pollution control system.

Industrial furnaces vary in their tolerance to inorganic constituents. Heavy metal concentrations, found in both halogenated and nonhalogenated wastes used as fuel, can cause environmental concern because they may be emitted in the gaseous emissions from the combustion process, in the ash residues, or in any produced solids. The partitioning of the heavy metals to these residual streams primarily depends on the volatility of the metal, waste matrix, and furnace design.

### 6.1.3 Heating Value of the Waste

The heating value of the waste must be high enough (either alone or in combination with other fuels) to maintain combustion temperatures consistent with efficient waste destruction and operation of the boiler or furnace. For many applications, only supplemental fuels having minimum heating values of 4,400 to 5,600 kcal/kg (8,000 to 10,000 Btu/lb) are considered to be feasible. Below this value, the unblended fuel would not be likely to maintain a stable flame, and its combustion would release insufficient energy to provide needed steam generation potential in the boiler or the necessary heat for an industrial furnace. Some wastes with heating values of less than 4,400 kcal/kg (8,000 Btu/lb) can be used if sufficient auxiliary fuel is employed to support combustion or if special designs are incorporated into the combustion device. Occasionally, for wastes with heating values higher than virgin fuels, blending with auxiliary fuel may be required to prevent overheating or overcharging of the combustion device.

### 6.1.4 Viscosity of the Waste

In combustion devices designed to burn liquid fuels, the viscosity of the liquid waste must be low enough that it can be atomized in the combustion chamber. If the viscosity is too high, heating the storage tanks may be required prior to combustion. For atomization of liquids, a viscosity of 165 centistokes (750 Saybolt Seconds Universal (SSU)) or less is typically required.

### 6.1.5 Filterable Solids Concentration

If filterable material suspended in the liquid fuel prevents or hinders pumping or atomization, it will be unacceptable.

### 6.1.6 Sulfur Content

A waste's sulfur content may affect whether it can be burned or not, because the waste may emit sulfur oxide into the atmosphere. For instance the EPA has proposed sulfur oxide emission regulations for certain new source industrial boilers (51 FR 22385). Air pollution control devices are available to remove sulfur oxides from the stack gases.

## 6.2 Underlying Principles of Operation

For a boiler and most industrial furnaces there are two distinct principles of operation. Initially, energy in the form of heat is transferred to the waste to achieve volatilization of the various waste constituents. For liquids, volatilization energy may also be supplied by using pressurized atomization. The energy used to pressurize the liquid waste allows the atomized waste to break into smaller particles, thus enhancing its rate of volatilization. The volatilized constituents then require additional energy to destabilize the chemical bonds, allowing the constituents to react with oxygen to form carbon dioxide and water vapor. The energy needed to destabilize the chemical bonds is referred to as the energy of activation.

## 6.3 Description of Fuel Substitution Process

Since a number of industrial applications can use fuel substitution, there is no one process description that will fit all of these applications. The following section, however, provides a general description of industrial kilns (one form of industrial furnace) and industrial boilers.

### 6.3.1 Kilns

Combustible wastes have the potential to be used as fuel in kilns and, for waste liquids, are often used with oil to co-fire kilns. Coal-fired kilns are capable of handling some solid wastes. In the case of cement kilns, there are usually no residuals requiring land disposal, since any ash formed becomes part of the product or is removed by particulate collection systems and recycled back to the kiln. The only residuals may be low levels of unburned gases that escape with combustion products. If this is the case, air pollution control devices may be required.

Three types of kilns are particularly applicable: cement kilns, lime kilns, and lightweight aggregate kilns.

(1) **Cement kilns**. The cement kiln is a rotary furnace, which is a refractory-lined steel shell used to calcine a mixture of calcium, silicon, aluminum, iron, and magnesium-containing minerals. The kiln is normally fired by coal or oil. Liquid and solid combustible wastes may then serve as auxiliary fuel. Temperatures within the kiln are typically between 1,380 and 1,540°C (2,500 to 2,800°F). To date, only liquid hazardous wastes have been burned in cement kilns.

Most cement kilns have a dry particulate collection device (i.e., either an electrostatic precipitator or a baghouse), with the fly ash collected recycled back to the kiln. Buildup of metals or other noncombustibles is prevented through their incorporation into the product cement. Many types of cement require a source of chloride so that most halogenated liquid hazardous wastes currently can be burned in cement kilns. Available information shows that scrubbers are not used.

(2) Lime kilns. Quick-lime (CaO) is manufactured in a calcination process using limestone ($CaCO_3$) or dolomite ($CaCO_3$ and $MgCO_3$). These raw materials are also heated in a refractory-lined rotary kiln, typically to temperatures of 980 to 1,260°C (1,800 to 2,300°F). Lime kilns are less likely to burn hazardous wastes than are cement kilns because product lime is often added to potable water systems. Only one lime kiln in the United States currently burns hazardous waste. That particular facility sells its product lime for use as flux or as refractory in blast furnaces.

As with cement kilns, any fly ash collected is recycled back to the lime kiln; thus, no residual streams are produced by the kiln. Available information shows that scrubbers are not used.

(3) Lightweight aggregate kilns. Lightweight aggregate kilns heat clay to produce an expanded lightweight inorganic material used in portland cement formulations and other applications. The kiln has a normal temperature range of 1,100 to 1,150°C (2,000 to 2,100°F). Lightweight aggregate kilns are less amenable to combustion of hazardous wastes as fuels than are the other kilns described above because these kilns lack material to adsorb halogens. As a result, burning of halogenated organics in these kilns would likely require afterburners to ensure complete destruction of the halogenated organics and scrubbers to control acid gas production. Such controls would produce a wastewater residual stream subject to treatment standards.

### 6.3.2 Industrial Boilers

A boiler is a closed vessel in which water is transformed into steam by the application of heat. Normally, heat is supplied by the combustion of pulverized coal, fuel oil, or gas. These fuels are fired into a combustion chamber with nozzles and burners that provide mixing with air. Liquid wastes, and granulated solid wastes in the case of grate-fired boilers, can be burned as auxiliary fuel in a boiler. Few grate-fired boilers burn hazardous wastes, however. For liquid-fired boilers, residuals requiring land disposal are generated only when the boiler is shut down and cleaned. This is generally done once or twice per year. Other residuals from liquid-fired boilers would be the gas emission stream, which would consist of any products of incomplete combustion, along with the normal combustion products. For example, chlorinated wastes would produce acid gases. If this is the case, air pollution control devices may be required. For solid-fired boilers, an ash normally is generated. This ash may contain residual amounts of organics from the blended waste/fuels, as well as noncombustible materials. Land disposal of this ash would require compliance with applicable BDAT treatment standards.

## 6.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether fuel substitution will achieve the same level of performance on an untested waste as on a previously tested waste, and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the component boiling points, (b) the thermal volutivily of the waste, and (c) the component bond dissociation energies.

### 6.4.1 Component Boiling Points

The term relative volatility ($\alpha$) refers to the ease with which a substance present in a solid or liquid waste will vaporize from that waste upon application of heat from an external source. Hence, it bears a relationship to the equilibrium vapor pressure of the substance.

EPA recognizes that the relative volatilities cannot be measured or calculated directly for the types of wastes generally treated in an industrial boiler or furnace. The Agency believes that the best measure of relative volatility is the boiling point of the various hazardous constituents and will, therefore, use this parameter in assessing volatility of the organic constituents.

### 6.4.2 Thermal Conductivity of The Waste

Consistent with the underlying principles of combustion in aggregate kilns or boilers, a major factor with regard to whether a particular constituent will volatilize is the transfer of heat through the waste. In the case of industrial boilers burning solid fuels, heat is transferred through the waste by three mechanisms: radiation, convection, and conduction. For a given boiler, it can be assumed that the type of waste will have a minimal impact on the heat transferred from radiation. With regard to convection, EPA believes that the range of wastes treated would exhibit similar properties with regard to the amount of heat transferred by convection. Therefore, EPA will not evaluate the radiation or convection heat transfer properties of wastes in determining similar treatability. For solids, the third heat transfer mechanism, conductivity, is the one principally operative or most likely to change between wastes.

Using thermal conductivity measurements as part of a treatability comparison for two different wastes through a given boiler or furnace is most meaningful when applied to wastes that are homogeneous. As wastes exhibit greater degrees of nonhomogeneity, thermal conductivity becomes less accurate in predicting treatability because the measurement essentially reflects heat flow through regions having the greatest conductivity (i.e., the path of least resistance) and not heat flow through all parts of the waste. Nevertheless, EPA has not identified a better alternative to thermal conductivity, even for wastes that are nonhomogeneous.

### 6.4.3 Component Bond Dissociation Energies

Given an excess of oxygen, an organic waste in an industrial furnace or boiler would be expected to convert to carbon dioxide and water vapor provided that the activation energy is achieved. Activation energy is the quantity of heat (energy) needed to destabilize molecular bonds so that the oxidation (combustion) reaction will proceed to completion. As a measure of activation energy, EPA is using bond dissociation energies. In theory, the bond dissociation energy would be equal to the activation energy; in practice, however, this is not always the case because of molecular interacdions bonds. In some instances, bond dissociation energies will not be available and will have to be estimated, or other energy effects will have a significant influence on activation energy.

## 6.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a fuel substitution system, EPA examines the following parameters: (a) combustion temperature, (b) residence time, (c) the degree of mixing, (d) air feed rate, (e) fuel feed rate, and (f) steam pressure/rate of production.

**(a) Combustion temperature.** Industrial boilers are generally designed based on their steam generation potential (Btu output). This factor is related to the design combustion temperature, which, in turn, depends on the amount of fuel burned and its Btu value. The fuel feed rates and combustion temperatures of industrial boilers are generally fixed based on the Btu values of fuels normally handled (e.g., No. 2 versus No. 6 fuel oils). When wastes are to be blended with fossil fuels for combustion, the blending, based on Btu values, must be such that the resulting Btu value of the mixture is close to that of the fuel value used in the design of the boiler. Industrial furnaces also are designed to operate at specific ranges of temperature in order to produce the desired product (e.g., lightweight aggregate). The blended waste/fuel mixture should be capable of maintaining the design temperature range.

(b) Residence time. A sufficient residence time of combustion products is normally necessary to ensure that the hazardous substances being combusted (or formed during combustion) are completely oxidized. Residence times on the order of a few seconds are generally needed at normal operating conditions. For industrial furnaces as well as boilers, the residence time is a function of the size of the furnace and the fuel feed rates. For most boilers and furnaces the residence time usually exceeds a few seconds.

(c) Degree of Mixing. Boilers are designed so that fuel and air are intimately mixed. This helps to ensure that complete combustion takes place. The shape of the boiler and the method of fuel and air feed influence the turbulence required for good mixing. Industrial furnaces also are designed for turbulent mixing where fuel and air are mixed.

(d) Air feed rate. An important operating parameter in boilers and many industrial furnaces is the oxygen content in the flue gas, which is a function of the air feed rate. Stable combustion of a fuel generally occurs within a specific range of air-to-fuel ratios. An oxygen analyzer in the combustion gases can be used to control the feed ratio of air to fuel to ensure complete thermal destruction of the waste and efficient operation of the boiler. When necessary, the air flow rate can be increased or decreased to maintain proper fuel-to-oxygen ratios. Some industrial furnaces do not completely combust fuels (e.g. coke ovens and blast furnaces); hence, oxygen concentration in the flue gas is a meaningless variable.

(e) Fuel feed rate. The rate at which fuel is injected into the boiler or industrial furnace will determine the thermal output of the system per unit of time (Btu/hr). If steam is produced, steam pressure monitoring will indirectly determine whether the fuel feed rate is adequate. However, various velocity and mass measurement devices can be used to monitor fuel flow directly.

(f) Steam pressure or rate of production. Steam pressure in boilers provides a direct measure of the thermal output of the system and is directly monitored by use of in-system pressure gauges. Increases or decreases in steam pressure can be effected by increasing or decreasing the fuel and air feed rates within certain operating design limits. Most industrial furnaces do not produce steam; instead they produce a product (e.g., cement, aggregate) and monitor the rate of production.

## 6.6 References

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# 7. INCINERATION

## 7.1 Applicability

Incineration is a treatment technology applicable to the treatment of wastes containing a wide range of organic concentrations and low concentrations of water, metals, and other inorganics. The four most common incineration systems are liquid injection, rotary kiln, fluidized bed, and fixed hearth.

Liquid injection incineration is applicable to wastes having sufficiently low viscosity values (less than 750 Saybolt Seconds Universal (SSU) such that the waste can be atomized in the combustion chamber. However, viscosity is temperature dependent so that while liquid injection may not be applicable to a waste at ambient conditions, it may become applicable when the waste is heated. In addition, the waste particles and the concentration of suspended solids need to be sufficiently low to avoid clogging of the burner nozzle (or atomizer openings).

Rotary kiln, fluidized and fixed hearth incineration are applicable to wastes having a wide range of viscosity, particle size, and suspended solids concentrations.

## 7.2 Underlying Principles of Operation

The basic principle of operations for incinerations is the thermal decomposition of organic constituents via cracking and oxidation reactions at high temperatures (usually between 760 and 1650°C (1400 and 3000°F) to convert them into carbon dioxide, water vapor, nitrite oxides, nitrates, and ammonia (for nitrogen-containing wastes), sulfur oxides and sulfate for sulfur containing wastes and halogen acids (for halogenated wastes).

In liquid injection incineration the organic constituents in the waste are volatilized and the chemical bonds are destabilized. Once the chemical bonds are broken, these constituents react with oxygen to form carbon dioxide, water vapor, and other aforementioned compounds. In rotary kiln and fixed hearth incineration, two chambers are involved in the incineration process.

In the primary chamber, the organic constituents in the waste are volatilized. During this volatilization process, some of the organic constituents oxidize to form carbon dioxide and water vapor. In the secondary chamber, the chemical bonds are destabilized resulting in the organic constituents reacting with oxygen to form carbon dioxide, water vapor, and other aforementioned compounds.

In fluidized bed incineration, one chamber contains the fluidizing sand and a freeboard section above the sand. The fluidized bed aids in the volatilizations and combustion of the organic waste constituents. The sand in the bed provides a sufficient heat capacity to the volatilization of organic constituents. The forced air used to fluidize the bed provides sufficient oxygen and turbulence to enhance the reactions of organics with oxygen to form carbon dioxide, water vapor, and other aforementioned compounds. Additional time for conversion of the organic constituents is provided by the freeboard above the fluidized bed.

## 7.3 Description of Incineration Processes

The physical form of the waste determines the appropriate feed method into the incineration systems. Liquids are pumped into the combustion chamber through nozzles or via specially designed atomizing burners. Wastes containing suspended particles may need to be screened to avoid clogging of small nozzle or atomizer openings. Sludges and slurries are fed using positive displacement pumps and water cooled injection ports.

Bulk solid wastes may require shredding for control of particles of particle size. They may be fed to the combustion chamber via rams, gravity feed, air lock feeders, vibratory or screw feeders, or belt feeders. Containerized waste is gravity- or ram-fed.

Although sustained combustion is possible with waste heat content as low as 2230 kcal/kg (Btu/lb), wastes are typically blended to a net heat content of 4450 kcal/kg (8000 Btu/kg) or higher or auxiliary fuel used in the combustion chambers to raise the heat content to appropriate levels to sustain the combustion process.

Following incineration of wastes, flyash particulates, and acid gases (halogen acids) and other gaseous pollutants (nitric oxides ($NO_x$) and sulfur oxides ($SO_x$)) are further treated in an air pollution control system. Particulate emissions from most waste combustion systems generally have particle diameters less than one micron and require high efficiency collection systems to minimize air emissions.

The most common air pollution control system used includes a quench (for gas cooling and conditioning), followed by a high-energy venturi scrubber* (for particulate and acid gas removal), a packed bed or plate tower absorber (for acid gas removal), and a demister (for vapor mist plume elimination).

Packed bed or plate tower scrubbers are commonly used without venturi scrubbers in the air pollution control systems at liquid injection incinerator facilities, where absorption of gaseous pollutants is more important than particulate control (because wastes burned in liquid injection incinerators typically have it low ash content and, hence, generate a low level of fly ash particulates).

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*A venturi is a short tube or duct with a tapering constriction that causes an increase in the velocity of fluid flow and a corresponding decrease in pressure.

Some liquid injection incinerator facilities do not employ any air pollution control system because the wastes burned contain low levels of both ash and halogen content, thereby generating low levels (i.e., untreatable) of fly ash particulates and acid gases.

Many air pollution control system designs in recent years have begun to incorporate waste heat boilers as a substitute for gas quenching as a means of energy recovery. Wet electrostatic precipitators (ESP), ionizing wet scrubbers (IWS), and fabric filters are also being incorporated into newer systems because of their high removal efficiencies for small particles and their lower pressure drop than venturi scrubbers.

The inorganic constituents of wastes (noncombustible ash) are not destroyed by incineration. These materials, depending on their composition, exit the incinerator as either bottom ash from the combustion chamber, or as fly ash particulates suspended in the combustion gas stream. Bottom ash is typically either air-cooled or quenched with water following discharge from the combustion chamber. This waste is then stabilized (if levels of leachable metal constituents or concern are found) and/or land disposed.

Fly ash particulates, as well as acid gases and other gaseous pollutants, are entrained in the scrubber waters of the air pollution control system and collected in sumps of recirculation tanks. Here the acids are neutralized with caustic and much of the water returned to the air pollution control system. Eventually, a portion or all of these scrubber waters is discharged for treatment and disposal when the total dissolved solids level becomes excessively high. Scrubber waters are discharged to either a settling tank or lagoon or to a chemical precipitation system (if treatable to levels of soluble metal constituents of concern are found) to remove these solids prior to their land disposal. Depending upon the nature of the remaining dissolved constituents and their concentrations allowing treatment, treated scrubber waters may be returned to the air pollution control system, further treated in filtration processes, or discharged.

Below are descriptions of the incineration processes for the four most common incinerator systems.

(a) Liquid injection. In a liquid injection incineration system, a burner or nozzle atomizes the waste and injects it into the combustion chamber where it is incinerated in the presence of air or oxygen. A forced draft system supplies the combustion chamber with air to provide oxygen for combustion and turbulence for mixing. The combustion chamber is usually a cylinder lined with refractory (i.e., heat resistant) brick and can be fired horizontally, vertically upward, or vertically downward. Figure 7-1 illustrates a diagram of a liquid injection incineration system.

(b) Rotary kiln. A rotary kiln is a slowly rotating, refractory-lined cylinder that is mounted at a slight incline from the horizontal. Solid wastes enter at the high end of the kiln, and liquid or gaseous wastes generally enter through atomizing nozzles in the afterburner section of the kiln. A forced draft system supplies the kiln with air to provide oxygen for combustion and turbulence for mixing. Rotation of the kiln enhances the exposure of the solids to the heat, thereby aiding their volatilization as well as principles for additional mixing of the solids with air combustion. In addition, the rotation causes the ash to move to the lower end of the kiln where it is removed. Rotary kiln systems usually have a secondary combustion chamber or afterburner following the kiln for further combustion of the volatilized waste constituents. Figure 7-2 presents a diagram of a rotary kiln incineration system.

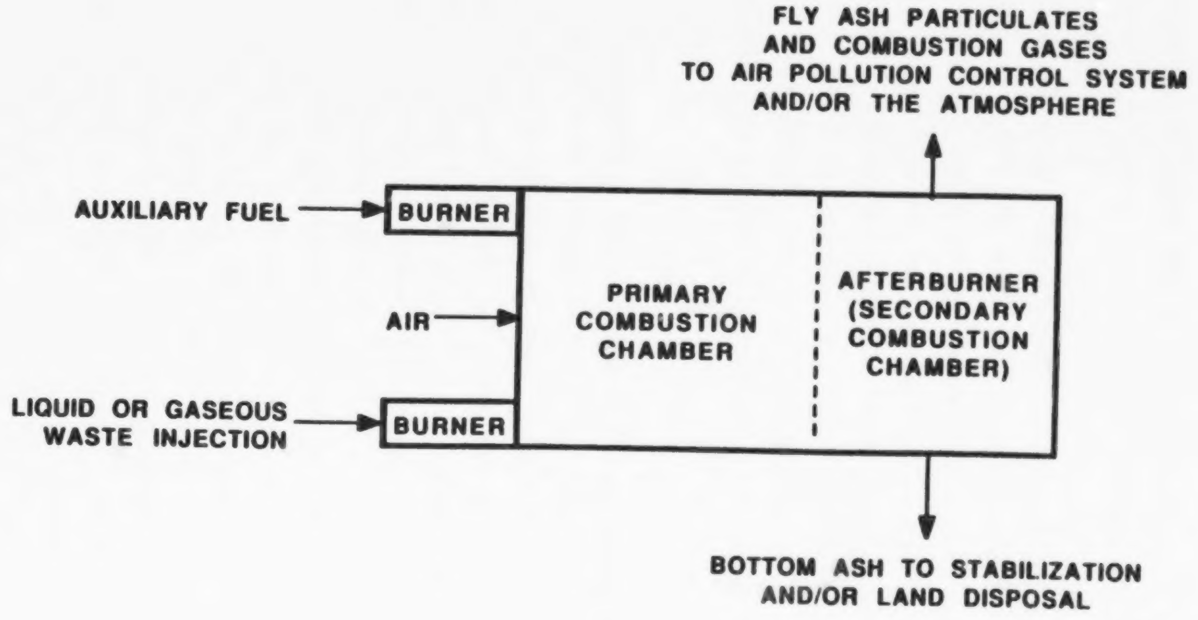
FLY ASH PARTICULATES
AND COMBUSTION GASES
TO AIR POLLUTION CONTROL SYSTEM
AND/OR THE ATMOSPHERE
AUXILIARY FUEL
BURNER
AIR
LIQUID OR GASEOUS
WASTE INJECTION
BURNER
PRIMARY
COMBUSTION
CHAMBER
AFTERBURNER
(SECONDARY
COMBUSTION
CHAMBER)
BOTTOM ASH TO STABILIZATION
AND/OR LAND DISPOSAL

Figure 7-1. Liquid Injection Incineration System.

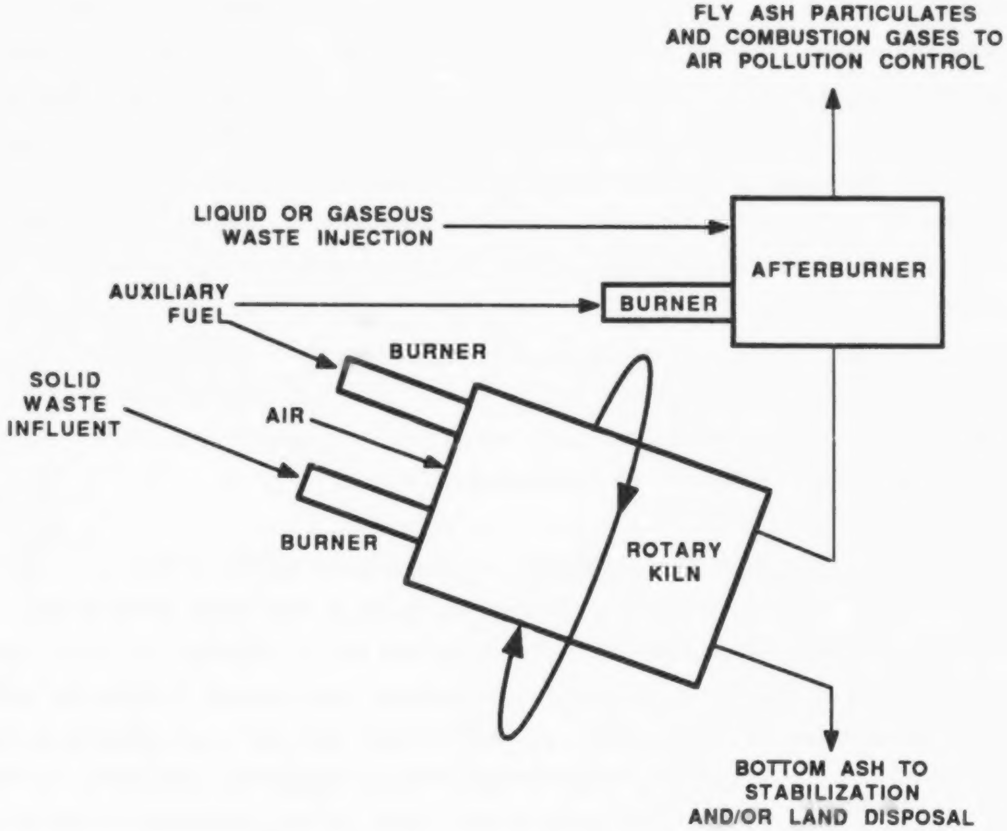
FLY ASH PARTICULATES AND COMBUSTION GASES TO AIR POLLUTION CONTROL
LIQUID OR GASEOUS WASTE INJECTION
AFTERBURNER
AUXILIARY FUEL
BURNER
BURNER
SOLID WASTE INFLUENT
AIR
BURNER
ROTARY KILN
BOTTOM ASH TO STABILIZATION AND/OR LAND DISPOSAL

Figure 7-2. Rotary Kiln Incineration System.

(c) **Fluidized bed**. A fluidized bed incinerator consists of a column containing inert particles such as sand which is referred to as the bed. Air, driven by a blower, enters the bottom of the bed to fluidize the sand. Air passage through the bed provides oxygen for combustion and promotes rapid and uniform mixing of the injected waste material within the fluidized bed. The fluidized bed has an extremely high heat capacity (approximately three times that of flue (combustion) gases at the same temperature), thereby providing a large heat reservoir. The injected waste reaches incineration temperature quickly and transfers the heat of combustion back to the bed. The freeboard above the fluidized bed provides additional time for combustion of organic constituents. Because of the excellent mixing properties associated with fluidized bed incinerators, they can operate at lower temperatures more effectively than other incinerators. Figure 7-3 shows a diagram of a fluidized bed incineration system.

(d) **Fixed hearth incineration**. Fixed hearth (also called controlled air or starved air) incineration is a two-stage combustion process. Waste is ram-fed into the first stage, or primary chamber, and burned at less than stoichiometric conditions (not enough oxygen suitable for complete combustion). The resultant smoke and pyrolysis products, consisting primarily of volatile hydrocarbons and carbon monoxide, along with the typical products of combustion, pass to the secondary chamber. Here additional air is injected to complete the combustion process. This two-stage process generally yields low fly ash particulate and carbon monoxide (CO) emissions. The primary chamber combustion reactions and resultant combustion gas velocities are maintained at low levels by the starved air conditions so that particulate entrainment and carryover in the combustion gases are minimized. Figure 7-4 is a diagram of a fixed hearth incineration system.

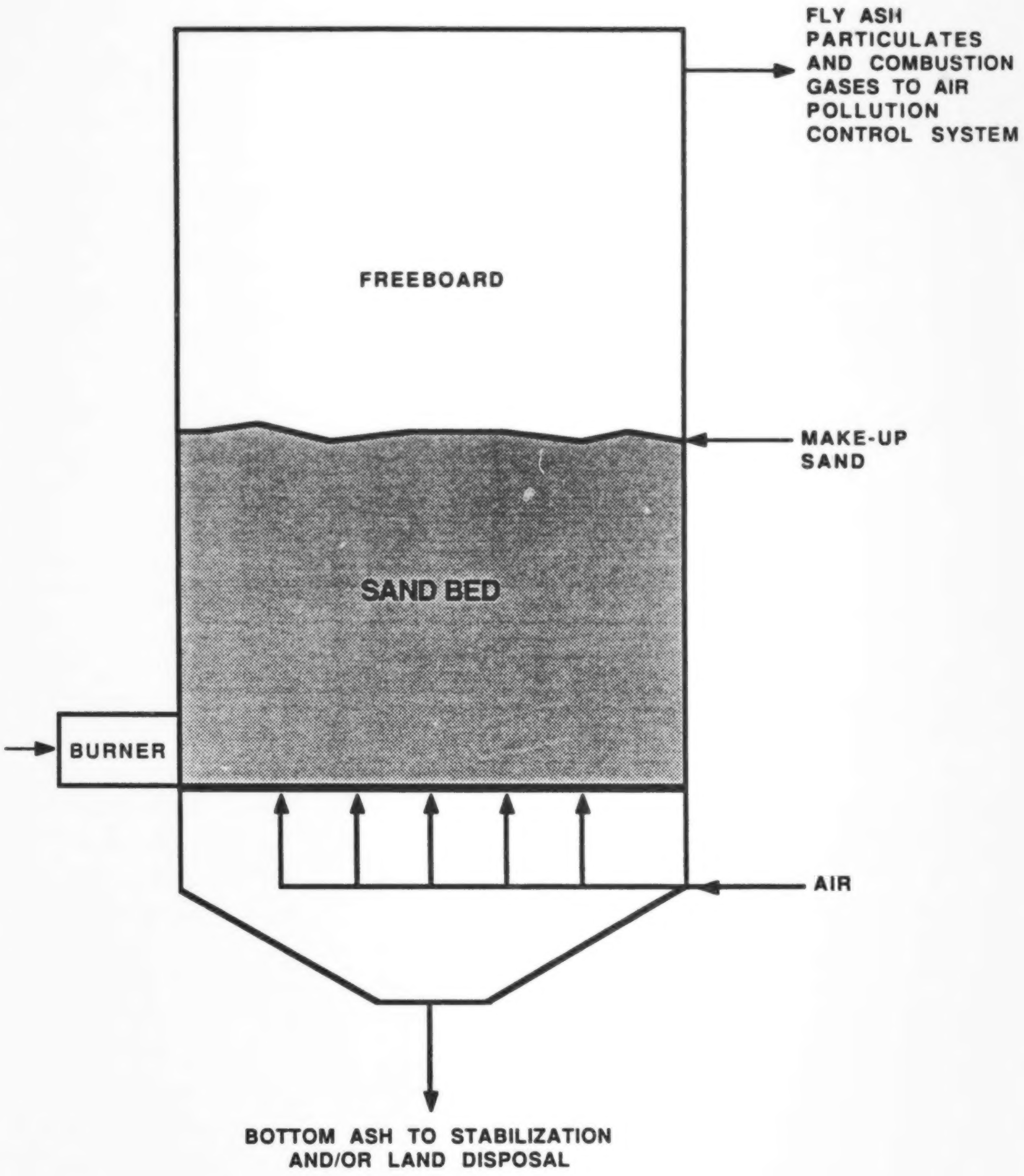
FLY ASH
PARTICULATES
AND COMBUSTION
GASES TO AIR
POLLUTION
CONTROL SYSTEM
FREEBOARD
MAKE-UP
SAND
SAND BED
BURNER
AIR
BOTTOM ASH TO STABILIZATION
AND/OR LAND DISPOSAL

Figure 7-3. Fluidized Bed Incineration System.

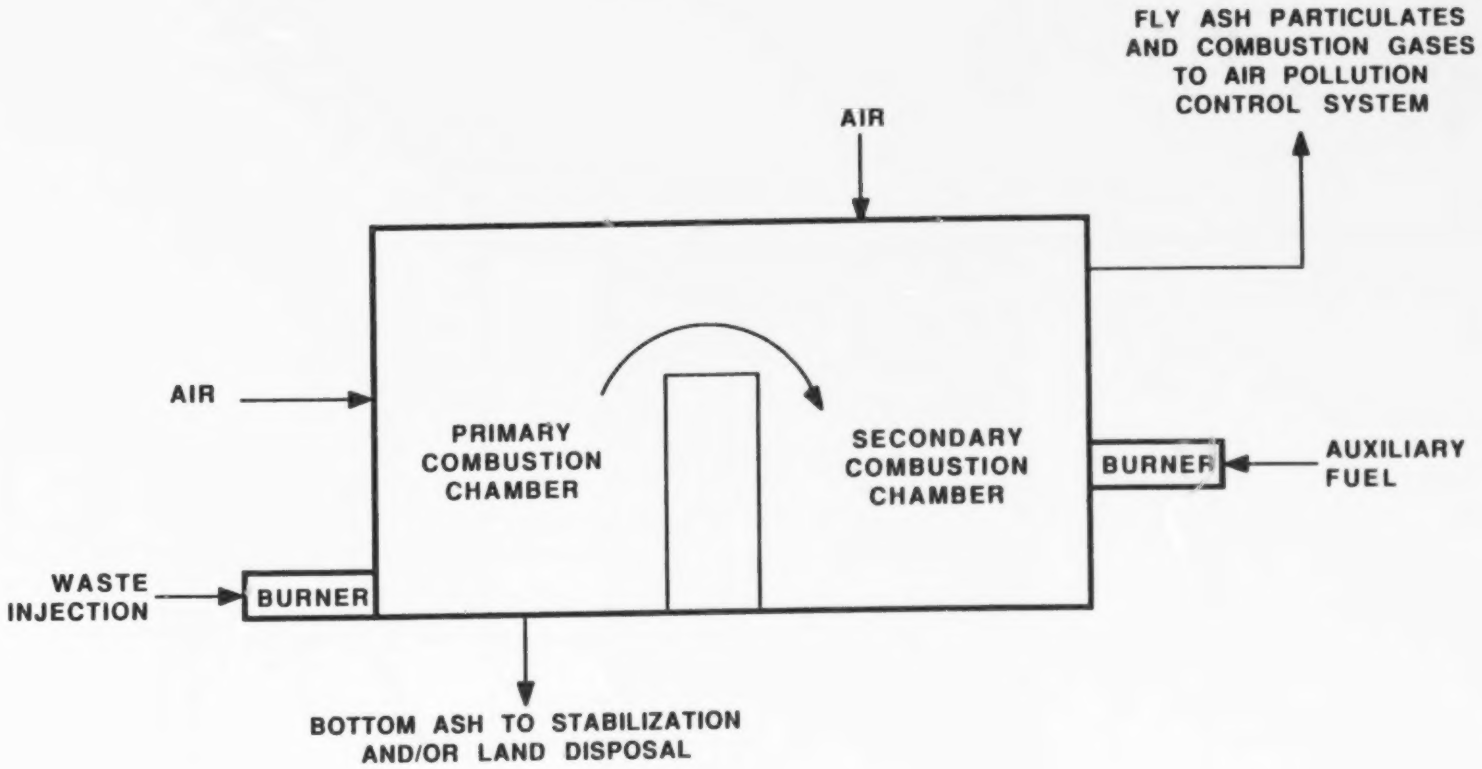
FLY ASH PARTICULATES
AND COMBUSTION GASES
TO AIR POLLUTION
CONTROL SYSTEM
AIR
AIR
PRIMARY
COMBUSTION
CHAMBER
SECONDARY
COMBUSTION
CHAMBER
BURNER
AUXILIARY
FUEL
WASTE
INJECTION
BURNER
BOTTOM ASH TO STABILIZATION
AND/OR LAND DISPOSAL

Figure 7-4. Fixed Hearth Incineration System.

## 7.4 Waste Characteristics Affecting Performance (WCAPS)

In determining whether incineration will achieve the same level of performance on an untested waste as on a previously tested waste, and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) The thermal conductivity of the waste, (b) The component boiling points, (c) The component bond dissociation energies, (d) The heating value of the waste, (e) The concentration of explosive constituents, and (f) The concentration of noncombustible constituents.

**(a) Thermal conductivity of the waste.** A major factor determining whether a particular constituent will volatilize is the transfer of heat through the waste. For rotary kiln, fluidized bed, and fixed hearth incineration, heat is transferred through the waste by radiation, convection, and conduction.

EPA examined all three methods of heat transfer. For a given incinerator, heat transferred through various wastes by radiation and convection is more a function of the design and type of incinerator that the waste being treated, therefore EPA believes that conduction would be the primary cause of heat transfer differences between wastes. Heat flow by conduction is proportional to the temperature gradient across the material. The proportionality constant is referred to as the thermal conductivity and is a property of the material to be incinerated.

Thermal conductivity measurements, as part of a treatability comparison for two different wastes to be treated by a single incinerator, are most meaningful when applied to wastes that are homogeneous (i.e., uniform throughout). As wastes exhibit greater degrees of non-homogenity, thermal conductivity becomes less accurate in predicting treatability because the measurement essentially reflects heat flow through regions having the greatest conductivity (i.e., the path of least resistance) and not heat flow through all parts of the waste. Nevertheless, EPA believes that thermal conductivity may provide the best measure of performance transfer. If the thermal conductivity of an untested waste is significantly lower than that of the tested waste, the system may not achieve the same performance. Higher temperatures may be required to improve heat transfer through the waste and achieve the same treatment performance, or other more applicable treatment technologies may need to be considered for treatment of the untested wastes.

(b) Component boiling points. Following transfer to a constituent within a waste, its removal depends on its volatility. EPA recognizes, however, that volatilities are difficult to measure or calculate directly for the types of wastes generally treated by incineration. This is because the wastes usually consist of a mixture of components. However, because the volatility of components is usually inversely proportional to their boiling points (i.e., the higher the boiling point, the lower the volatility). EPA uses the boiling of waste components as a surrogate waste characteristic for volatility. If the boiling points of waste components in the untested waste are significantly higher than in the tested waste, the system may not achieve the same performance. Higher temperatures may be required to volatilize less volatile components and achieve the same treatment performance or other, more applicable treatment technologies may need to be considered for treatment of the untested wastes.

(c) Component bond dissociation energies. The activation energy is the amount of heat energy needed to destabilize molecular bonds so that the exothermic combustion reactions can proceed. Generally, the activation energy required for incineration of solids is greater than required for liquids; and the activation energy for liquids is higher than for gases. However, the activation energies for components are difficult to measure or calculate directly, and generally have to be determined empirically. The bond dissociation energy is the amount of energy needed to break each of the individual bonds in a molecule. Theoretically, the bond dissociation energy and the activations energy are equivalent. However, other energy effects including interactions between different molecular bonds may have a significant influence on the activation energy. Nevertheless, EPA believes that bond dissociation energy is the best indicator for activation energy and therefore, uses it as a surrogate waste characteristic. If the bond dissociation energies of waste components in an untested waste are significantly higher than in the tested waste, the system may not achieve the same performance. Higher temperatures may be required to destabilize molecular bonds for waste components with high bond dissociation energies and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

(d) Heating value of the waste. The amount of heat released from the exothermic combustion reactions of a waste is referred to as its heating value. To maintain combustion, the heating value of a waste must be sufficient to heat incoming waste up to the appropriate design incineration temperature and provide the necessary activation energy for additional combustion reactions to occur. Higher waste heating values are required for higher incineration temperatures and higher amounts of excess oxygen to sustain combustion without auxiliary fuel consumption. Low heating values for an organic waste are usually caused by high concentrations of water or halogenated compounds. If the heating value of an untested waste is significantly lower than of the tested waste, the system may not achieve the same performance. Auxiliary fuel may be required to provide the necessary heat to maintain combustion and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

(e) Concentration of explosive constituents. Explosive constituents may interfere with the smooth operation of an incinerator causing process upsets resulting in ineffective treatment of the waste. If the concentration of explosive constituents in an untested waste is significantly higher than in the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

(f) Concentration of noncombustible constituents. Noncombustible constituents include water, metals, and other inorganics. High concentrations of noncombustible constituents result in low waste heating values requiring auxiliary fuel large quantities of bottom ash requiring stabilization treatment (if treatable levels of leachable metal constituents of concern are present) and/or disposal, and large quantities of fly ash particulates and volatile metals in the combustion gases requiring removal in an air pollution control system and treatment in a settling tank or lagoon, or a chemical precipitation system (if treatable levels of soluble metal constituents of concern are present) followed by disposal. Volatile metals such as arsenic may also fuse to the refractory walls in the combustion chamber inhibiting effective operation of the incinerator. If the concentration of noncombustible constituents in an untested waste is significantly higher than in the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 7.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of an incineration system, EPA examines the following parameters: (a) the incineration temperature, (b) the concentration of excess oxygen in the combustion gas, (c) the concentration of carbon monoxide in the combustion gas, (d) the waste feed rate, and (e) the degree of waste/air mixing.

(a) Incineration temperature. Temperature provides an indirect measure of the energy available (i.e., Btu/hr) to both volatilize organic waste constituents and overcome their activation energy. As the design temperature in the combustion chamber increases, more constituents with lower volatilities and higher activation energies will be destroyed. EPA monitors the incinerations temperature continuously, to ensure that the system is operating at the appropriate design conditions and to diagnose operational problems.

(b) Concentrations of excess oxygen in the combustion gas. A sufficient supply of oxygen needs to be supplied to the combustion chamber to effectively incinerate the organic waste constituents. The stoichiometric or minimum theoretical oxygen requirement to completely combust the waste is based on the amounts of combustible constituents in the waste. If perfect mixing could be achieved and the waste burned instantaneously, only the stoichiometric amount of oxygen would be needed for complete combustion. However, neither of these phenomena occur in commercial incinerators. The amount of excess oxygen in a given incinerator depends on the degree of waste/air mixing achieved in the combustion chamber and the desired degree of combustion gas cooling. Because excess air (oxygen) supplied to the combustion chamber acts as a diluent in the combustion process, it reduces the overall temperature in the incinerator (i.e., maximum theoretical incineration temperatures are achieved at zero percent excess air). This temperature reduction might be desirable to limit refractory degradation when high heating value wastes are being burned. However, when low heating value wastes are being burned, excess air should be minimized to keep the system temperature as high as possible. Even with high heating value waste, it is desirable for equipment design considerations to limit the amount of excess air to some extent so that combustion chamber volume and downstream air pollution control system sizes can be limited.

Although, an inadequate supply of oxygen will lead to ineffective incineration with higher concentrations of carbon monoxide (CO) and organic products of incomplete combustion (PICs), resulting in a heavier load on the air pollution control system. Typically, 20 to 60 percent excess oxygen is required to provide adequate waste/oxygen contact and, subsequently, effective incineration of the waste. EPA monitors the concentration of excess oxygen in the combustion gas continuously to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

(c) Concentration of carbon monoxide in the combustion gas. The concentration of carbon monoxide in the combustion gas provides an indication of the extent to which organic waste constituents are converted to carbon dioxide and water vapor. Higher carbon monoxide levels ineffective incineration with the presence of greater amounts of unreacted or partially reacted organic waste constituents in the combustions gas, resulting in a heavier load on the air pollution control system. Higher carbon monoxide levels can result from an insufficient incineration temperature, an inadequate supply of excess oxygen, a waste feed rate that is too high resulting in an insufficient residence time for the waste, and improper mixing in the combustions chamber. EPA monitors the concentration of carbon monoxide in the combustion gas continuously to ensure that the system is operating at the appropriate design conditions and to diagnose operational problems.

(d) Waste feed rate. The waste feed rate determines the residence time of the waste in the combustion chamber. Sufficient residence time must be provided to allow for volatilization of the organic waste constituents, mixing with oxygen in the combustions chamber, and completion of the combustion reactions. The total residence time required for these processes to occur depends on the incineration temperature, the amount of excess oxygen provided in the combustion chamber, the degree of waste/air mixing in the combustion chambers, the size and type of incinerator used, the physical form of the waste, and the waste particle size (which determines the amount of waste surface areas available for heat transfer). Typical incinerator residence times range from approximately 2 seconds for liquid and gaseous wastes in liquid injection incinerators and the afterburner, freeboard, and secondary combustions chamber of rotary kiln, fluidized bed, and fixed hearth incinerators, respectively, to 30 minutes to 1 hour for solid wastes in a rotary kiln incinerator. EPA monitors the waste feed rate continuously to ensure that sufficient residence time is provided to effectively incinerate organic waste constituents.

(e) Degree of waste/air mixing. The incineration temperature, the amounts of excess oxygen, and the residence time required to achieve effective incineration of a waste all depend to some extent on the degree of waste/air mixing in the combustion chamber. For liquid injection incinerators, the degree of waste/air mixing is primarily determined by the specific burner design and the degree of atomization achieved of the waste/air mixture. The degree of atomization is dependent on the viscosity of the liquid waste and the amount of solid impurities present. If the waste viscosity exceeds 750 SSU or the amount of solid impurities is too high, the degree of atomization may not be fine enough resulting in ineffective incineration.

For rotary kiln incineration, the degree of waste/air mixing is determined by the air flow rate into the kiln as well as the rate of rotation (revolutions per minute (RPM)) of the kiln. As the air flow rate is increased, the degree of waste/air mixing is improved. Although this also reduces the incineration temperature and residence time the combustion gases. Increasing the rate of rotations of the kiln also improves waste/air mixing. However, the waste solids' residence time is also reduced. Typical rotation rates for rotary kilns range from 0.3 to 1.5 meters per minute (1 to 5 feet per minute).

For fluidized bed incineration, the degree of waste/air mixing is indicated by the pressure drop through the bed caused by the air flow rate used to fluidize the bed. The higher the pressure drop, the greater the degree of mixing in the fluidized bed. However, this also reduces the incineration temperature and the residence time of the waste solids and combustion gases.

For fixed hearth incineration, the degree of waste/air mixing is determined by the air flow rate into the combustion chamber. As the air flow rate is increased, the degree of waste/air mixing is improved. However, this also reduces the incineration temperature and the residence time of the combustion gases.

The quantifiable degree of waste/air mixing is a complex assessment which is difficult to express in absolute terms. However, for liquid injection incineration, EPA evaluates the degree of mixing qualitatively by examining the burner design and determining whether it could be expected to achieve effective atomization of the waste/air mixture. For rotary kiln incineration, EPA estimates the degree of mixing by monitoring the air flow rate into the kiln as well as the kiln's rate of rotation to ensure that effective mixing of the waste and air is achieved. For fluidized bed incineration, EPA estimates the degree of mixing by monitoring the pressure drop through the bed to ensure that effective mixing of waste and air is achieved. For fixed hearth incineration, EPA estimates the degree of mixing by monitoring the air flow rate into the combustion chamber to ensure that effective mixing of the waste and air is achieved.

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# 8. SOLVENT EXTRACTION

## 8.1 Applicability

Solvent extraction is a treatment technology used to treat wastes with a broad range of total organic content, with the selection of a solvent dependent upon its solubility with the organic compounds to be removed and the other constituents in the waste. This technology has been used to treat oil refinery wastes and other organic wastes.

## 8.2 Underlying Principles of Operation

The basic principle of operation in solvent extraction is that constituents are removed from a waste by mixing the waste with a solvent that will preferentially dissolve the waste constituents of concern from the waste. The waste and the solvent must be immiscible so that after mixing the two immiscible phases can physically separate by gravity. In theory, the maximum degree of separation that can be achieved is provided by the selectivity value, which is the ratio of the equilibrium concentration of the constituent in the solvent to the equilibrium concentration of the constituent in the waste. The solvent extraction process can be either batch or continuous.

In the simplest extraction systems, three chemical components are mixed: (1) the solute, or the constituents in the waste stream to be extracted; (2) the nonsolute portion of the waste stream; and (3) the solvent. The solvent and the waste stream are mixed to allow mass transfer of the constituent(s) (the solute) from the waste stream to the solvent. Separation of the solvent phase and the waste stream phase occurs under quiescent conditions, relying on the density differences between the two phases.

The solvent solution containing the extracted contaminants is called the extract, and the extracted waste stream with the contaminants removed is called the raffinate. The extract can be either the heavy (more dense) phase or the light (less dense) phase.

## 8.3 Description of Solvent Extraction Processes

The simplest, least effective solvent extraction unit is a single-stage system (mixer-settler system). The solvent and the liquid waste stream are mixed together; the raffinate and extract are separated by settling without further extraction.

The more effective multistage contact extraction is basically a series of mixer-settler units. The waste stream is contacted with solvent in a series of successive steps or stages. Raffinate from the first extraction stage is contacted with fresh solvent in a second stage, and so on.

In countercurrent, multistage extraction columns, fresh solvent and the waste stream enter at opposite ends of a column consisting of a series of extraction stages. Extract and raffinate layers pass continuously and countercurrently from stage to stage through the system.

Several types of extraction systems are used for contact and separation. Three of the most common systems--mixer-settler systems, extraction columns, and centrifugal contactors--are discussed below.

### 8.3.1 Mixer-Settler Systems

Single-stage mixer-settler systems are extraction systems composed of a mixing chamber for phase dispersion, followed by a settling chamber for phase separation. Mixer-settler systems are typically used to treat solids or highly viscous wastes and can handle difficult dispersion systems. The vessels may be either vertical or horizontal. Dispersion in the mixing chamber occurs by pump circulation, nonmechanical in-line mixing, air agitation, or mechanical stirring.

In a two-stage mixer-settler system (a simple multistage contact extractor), as shown in Figure 8-1, the extract from the first stage is sent to a recovery unit to separate the solvent from the remaining extract containing the organic constituents of concern. The recovered solvent is used, and the remaining extract is either reused or further treated in an incineration unit. The raffinate from the first stage is sent to the second-stage unit for additional extraction. Recycled solvent from recovery of the first-stage extract and/or fresh solvent makeup is added to the first-stage raffinate before it is mixed and sent to the second-stage. The extract from the second stage, containing mainly solvent, is recycled to the first-stage unit as the solvent stream. The resulting raffinate from the second stage may require filtering to remove solids before it is sent to further treatment if required. Any solids collected during filtration are land disposed unless they contain treatable levels of hazardous constituents. If they do contain treatable levels of hazardous constituents, they will require further treatment, such as stabilization (for metals) and/or incineration (for organics).

Parameters such as the density or specific constituent concentrations in the extract may be monitored to determine when the second stage extract must be sent to solvent recovery and when fresh or recycled solvent must be added to the first-stage unit.

### 8.3.2 Extraction Columns

Extraction columns are countercurrent, multistage contact systems. Two types of extraction columns are packed extractors and sieve-tray

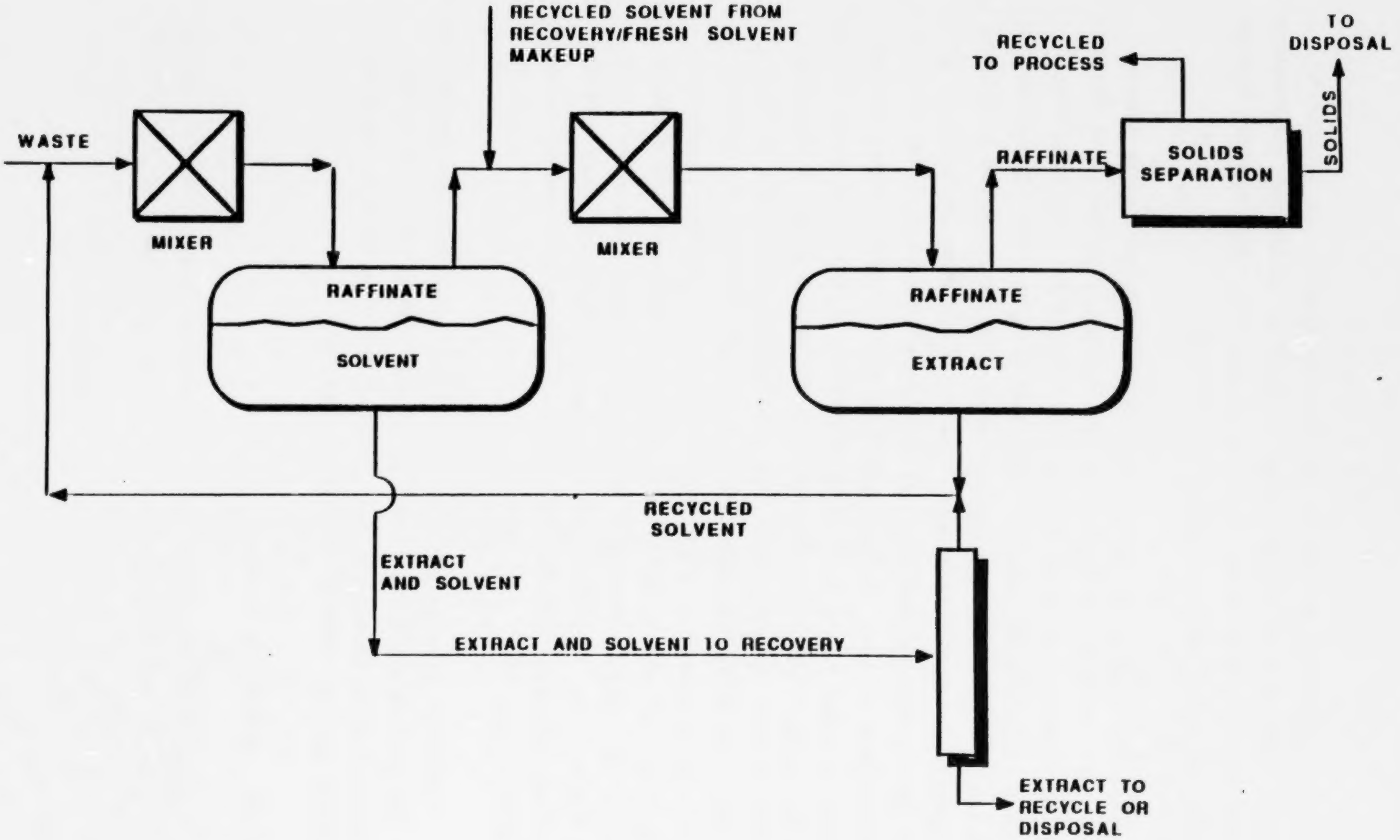

RECYCLED SOLVENT FROM RECOVERY/FRESH SOLVENT MAKEUP
WASTE
MIXER
MIXER
RAFFINATE
SOLVENT
RAFFINATE
EXTRACT
RECYCLED TO PROCESS
TO DISPOSAL
RAFFINATE
SOLIDS SEPARATION
SOLIDS
RECYCLED SOLVENT
EXTRACT AND SOLVENT
EXTRACT AND SOLVENT TO RECOVERY
EXTRACT TO RECYCLE OR DISPOSAL

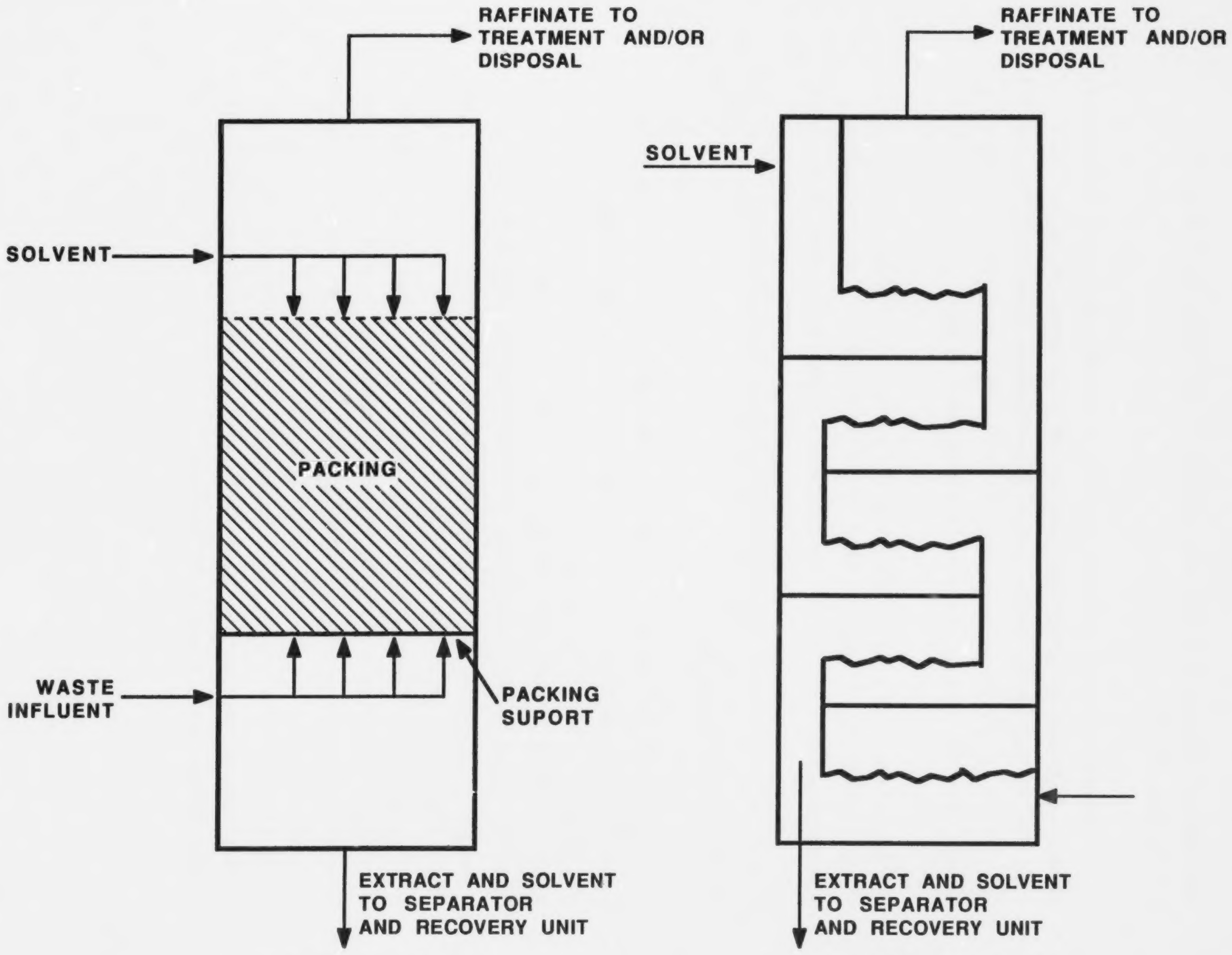
FIGURE ~~15-1~~ 8-1 TWO-STAGE MIXER-SETTLER SOLVENT EXTRACTION SYSTEM extractors. Figure 8-2 presents schematics of these two types of extraction columns.

A packed extractor contains plastic or ceramic materials in various geometric shapes or structured packings of wire gauze or mesh. Mass transfer of the solute to the extract is promoted because of breakup and distortion of the dispersed phase as it contacts the packing, resulting in the intimate mixing of the solute and the solvent.

The sieve-tray extractor is similar to the sieve-tray column used in fractionation distillation. Tray perforations produce the formation of liquid droplets that aid the mass transfer process by allowing for more intimate contact between the solute and the solvent.

### 8.3.3 Centrifugal Contactors

Centrifugal contactors are based on the application of centrifugal force to increase rates of countercurrent flow and enhance separation of the phases. Centrifugal units are used when short contact times are required, such as when unstable materials are being processed. One type of centrifugal contactor consists of a drum that rotates around a shaft equipped with annular passages at each end for feed and raffinate. The light phase is injected under pressure through a shaft and is then routed to the periphery of the drum through perforations. The heavy phase is also charged through the shaft, but it is channeled to the center of the drum through perforations. Centrifugal force acting on the phase-density difference promotes dispersion as the phases are forced through the perforations. Centrifugal extractors provide short contact time, have minimal space requirements, and easily handle emulsified materials and fluids having small density differences.


RAFFINATE TO
TREATMENT AND/OR
DISPOSAL
SOLVENT
PACKING
WASTE
INFLUENT
PACKING
SUPORT
EXTRACT AND SOLVENT
TO SEPARATOR
AND RECOVERY UNIT
RAFFINATE TO
TREATMENT AND/OR
DISPOSAL
SOLVENT
EXTRACT AND SOLVENT
TO SEPARATOR
AND RECOVERY UNIT

A. PACKED EXTRACTOR

B. SIEVE TRAY EXTRACTOR

Figure 8-2. Packed and Sieve Tray Solvent Extraction Columns.

## 8.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether solvent extraction will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the concentration of extractable hydrocarbons, (b) the solubility of the waste constituents of concern in the solvent, and (c) the surface tension.

### 8.4.1 Concentration of Extractable Hydrocarbons

The concentration of extractable hydrocarbons in the waste feed is a measure of the maximum fraction of the waste that can be expected to be extracted in the solvent extraction process. A relatively low concentration of extractable hydrocarbons implies that most of the waste may become raffinate or waste solids (i.e., is nonextractable). Total extractable hydrocarbon content can be estimated by measurement of the total organic carbon (TOC) content. If the TOC of an untested waste is significantly lower than that of the tested waste, the system may not achieve the same performance. More rigorous extraction conditions such as higher temperatures and pressures, additional mixing, and longer settling times may be required to extract less extractable components and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 8.4.2 Solubility of the Waste Constituents of Concern in the Solvent

The constituents in the waste feed that are to be extracted determine the type of solvent that is best suited for the extraction process. For example, polar molecules in an organic feed can be extracted with an aqueous solvent. Conversely, organic constituents in aqueous feeds can be extracted with organic solvents. Metal-containing wastes may be extracted with organic acids (e.g., trialkylphosphoric, sulfuric, and carboxylic acids) or amine solvents. If the solubility of the waste constituents of concern in the solvent in the untested waste is significantly lower than that in the tested waste, the system may not achieve the same performance. Use of another solvent may be required to increase the solubility of the waste constituents of concern and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 8.4.3 Surface Tension

The surface tension of the waste is a measure of the tendency of the waste to foam. The higher the surface tension of the liquid, the higher its tendency to foam. If foaming is likely, the system design must be modified or defoaming compounds may be required. For column extractors, packed columns are less susceptible to foaming than tray columns. If the surface tension of the untested waste is significantly higher than that of the tested waste, the system may not achieve the same performance. Defoaming compounds and/or the use of a packed column may be required to reduce foaming and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 8.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a solvent extraction system, EPA examines the following parameters: (a) the number of separation stages, (b) the extraction temperature and pH, (c) the degree of mixing, (d) the residence time, and (e) the settling time.

### 8.5.1 Number of Separation Stages

For extraction columns, the number of theoretical stages required to achieve the desired separation of hazardous constituents from a liquid waste into the selected solvent is calculated from solvent equilibrium data, which are determined empirically. Using the theoretical number of stages, the actual number of stages can then be determined through the use of empirical tray efficiency data typically supplied by an equipment manufacturer. EPA examines the actual number of stages in a solvent extraction column system to ensure that the system is designed to achieve an effective degree of extraction.

### 8.5.2 Extraction Temperature and pH

Temperature and pH changes can affect equilibrium conditions and, consequently, the performance of the extraction system. EPA monitors the temperature and pH continuously, if possible, to ensure that the system is operated at the appropriate design conditions and to diagnose operational problems.

### 8.5.3 Degree of Mixing

For mixer-settler extractors, mixing determines the amount of contact between the two immiscible phases and, accordingly, the degree of mass transfer of the constituents to be extracted. Intense agitation to provide high rates of mass transfer, however, can produce solvent waste dispersions that are difficult to separate into distinct phases. The quantifiable degree of mixing is a complex assessment that includes, among other things, the amount of energy supplied, the length of time the material is mixed, and the related turbulence effects of the specific size and shape of the tank vessel. This is beyond the scope of simple measurement. EPA, however, evaluates the degree of mixing qualitatively by considering whether the type of mixing device provided is one that could be expected to achieve uniform mixing of the waste.

### 8.5.4 Residence Time

The residence time in the extraction vessel impacts the extent of extraction of organic contaminants from the waste. It is dependent on the solubility of the organic contaminants in the solvent. For a batch system, the residence time is controlled directly by adjusting the treatment time in the extraction vessel. For a continuous system, the waste feed rate is controlled to ensure that the system is operating at the appropriate design residence time. EPA monitors the residence time to ensure that sufficient time is provided to effectively extract the organic contaminants from the waste.

### 8.5.5 Settling Time

For mixer-settler extractors, adequate settling time must be provided to make sure that separation of the phases has been effectively completed. EPA monitors the settling time to ensure effective phase separation.

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# 9. STEAM STRIPPING

## 9.1 Applicability

Steam stripping is a form of distillation applicable to the treatment of wastewaters containing organics that are volatile enough to be removed by the application of heat using steam as the heat source. Typically, steam stripping is applied where there is less than 1 percent volatile organics in the waste.

## 9.2 Underlying Principles of Operation

The basic principle of operation for steam stripping is the volatilization of hazardous constituents through the application of heat. The constituents that are volatilized are then condensed and typically either reused or further treated by liquid injection incineration.

An integral part of the theory of steam stripping is the principle of vapor-liquid equilibrium. When a liquid mixture of two or more components is heated, the vapor phase present above the liquid phase becomes more concentrated in the more volatile constituents (those having higher vapor pressures). The vapor phase above the liquid phase is then cooled to yield a condensate that is also more concentrated in the more volatile components. The degree of separation of components depends on the relative differences in the vapor pressures of the constituents; the larger the difference in the vapor pressures, the more easily the separation can be accomplished.

If the difference between the vapor pressures is extremely large, a single separation cycle or a single equilibrium stage of vaporization and condensation may achieve a significant separation of the constituents

(Typically, batch distillation or thin film evaporation would be used in such a case.) If the difference between the vapor pressures is small, then multiple equilibrium stages are needed to achieve effective separation. In practice, the multiple equilibrium stages are obtained by stacking trays or placing packing into a column. Essentially, each tray represents one equilibrium stage. In a packed steam stripping column, the individual equilibrium stages are not discernible, but the number of equivalent trays can be calculated from mathematical relationships using the height of the packing. The vapor phase from a tray rises to the tray above it, where it condenses; the liquid phase falls to the tray below it, where it is again heated and separated.

The vapor-liquid equilibrium of the waste components can be expressed as relative volatility, which is the ratio of the vapor-to-liquid concentrations of a constituent divided by the ratio of the vapor-to-liquid concentrations of another constituent. The relative volatility is a direct indicator of the ease of separation. If the numerical value is 1, then separation is impossible because the constituents have the same concentrations in the vapor and liquid phases. When the relative volatility is 1, the liquid mixture is called an azeotrope. Separation becomes easier as the value of the relative volatility becomes increasingly different from unity.

## 9.3 Description of Steam Stripping Process

A steam stripping unit consists of a boiler, a stripping column, a condenser, and a collection tank, as shown in Figure 9-1. The boiler provides the heat required to vaporize the liquid fraction of the waste. The stripping column is composed of a set of trays or packing placed in a vertical column.

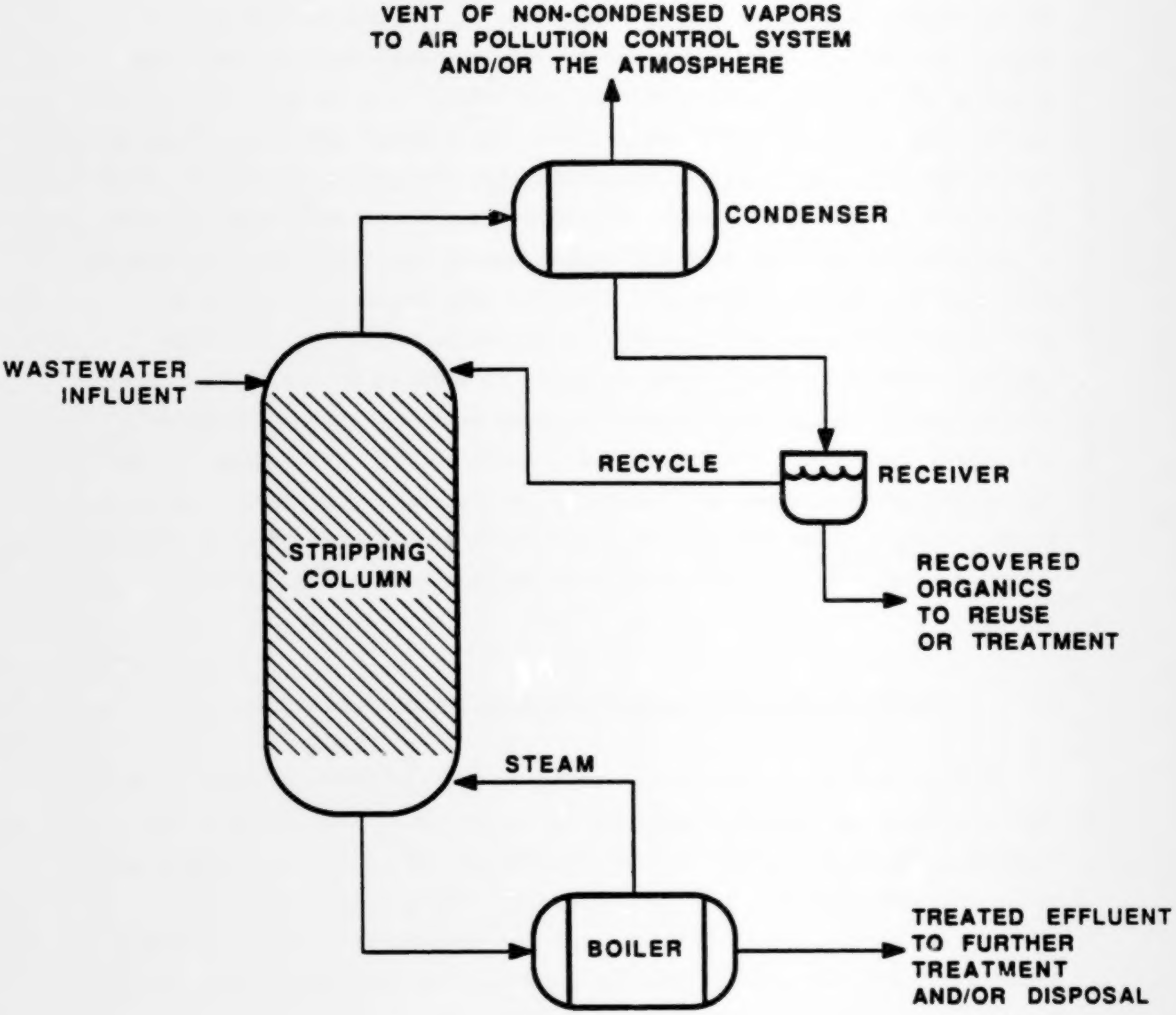
VENT OF NON-CONDENSED VAPORS
TO AIR POLLUTION CONTROL SYSTEM
AND/OR THE ATMOSPHERE
CONDENSER
WASTEWATER
INFLUENT
RECYCLE
RECEIVER
STRIPPING
COLUMN
RECOVERED
ORGANICS
TO REUSE
OR TREATMENT
STEAM
BOILER
TREATED EFFLUENT
TO FURTHER
TREATMENT
AND/OR DISPOSAL

**Figure 9-1. Steam Stripping System.**

The stripping process uses multiple equilibrium stages, with the initial waste mixture entering at the top, the uppermost equilibrium stage. The boiler is located beneath the lowermost equilibrium stage, allowing the vapor to move upward in the column, coming into contact with the falling liquid. As the vapor comes into contact with the liquid at each stage, the more volatile components are removed or "stripped" from the liquid by the vapor phase. The concentration of the emerging vapor is enriched in the more volatile constituents, and the liquid exiting the bottom of the boiler ("bottoms") contains high concentrations of the lower vapor pressure constituents, often predominately water. This effluent from the bottom of the stripper is reduced in organic content but may still require additional treatment such as carbon adsorption or biological treatment. The steam and organic vapors exiting the top of the column are condensed and separated in a product receiver. Organics in the organic phase are typically recovered or disposed of in a liquid injection incinerator. The aqueous condensate is recycled to the stripper.

## 9.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether steam stripping will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the component boiling points, (b) the concentration of suspended solids, (c) the concentration of volatile components, (d) the surface tension, and (e) the concentration of oil and grease.

### 9.4.1 Component Boiling Points

As noted earlier, the greater the ratio of volatility of the waste constituents, the more easily the separation of these constituents can proceed. This ratio is called relative volatility. EPA recognizes, however, that relative volatilities cannot be measured or calculated directly for the complex types of wastes generally treated by steam stripping. This is because the wastes usually consist of a myriad of components, all with different vapor pressure-versus-temperature relationships. Determining relative volatilities is further complicated by the fact that the relative volatility changes as the temperature conditions change throughout the steam stripping column (the column is cooler at the top than at the bottom). However, because the volatility of components is usually inversely proportional to their boiling points (i.e., the higher the boiling point, the lower the volatility), EPA uses the boiling point of waste components as a surrogate waste characteristic for relative volatility. If the differences in boiling points between the more volatile and less volatile (water) constituents are significantly lower in the untested waste than those in the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 9.4.2 Concentration of Suspended Solids

Wastes containing large amounts of suspended solids, organic or inorganic, may clog column internals and coat heat transfer surfaces, thereby inhibiting mass transfer of constituents between the vapor and liquid phases. If the concentration of suspended solids in the untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance. Filtration may be required prior to steam stripping to reduce the concentration of suspended solids and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 9.4.3 Concentration of Volatile Components

The concentration of volatile components is a measure of the maximum fraction of the waste that can be expected to volatilize in the steam stripping column. An extremely high concentration of volatile components may imply that adequate separation will not occur. If the concentration of volatile components in the untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance. Higher temperatures, lower pressures, and/or an increase in the number of separation stages may be required to volatilize less volatile compounds and achieve the same treatment performance, or other, more applicable technologies may need to be considered for treatment of the untested waste.

### 9.4.4 Surface Tension

The surface tension of the waste is a measure of the tendency of the waste to foam. The higher the surface tension of the liquid, the higher its tendency to foam. The likelihood of foaming requires special column design or the incorporation of defoaming compounds. If the surface tension of the untested waste is significantly higher than that of the tested waste, the system may not achieve the same performance. Defoaming compounds and/or the use of a packed column may be required to reduce foaming and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 9.4.5 Concentration of Oil and Grease

High concentrations of oil and grease may clog steam stripping equipment, thereby reducing its effectiveness. If the concentration of oil and grease in the untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 9.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a steam stripping system, EPA examines the following parameters: (a) the number of separation stages, (b) the liquid and vapor flow rates, (c) the stripping temperature and pressure, and (d) the internal column design.

### 9.5.1 Number of Separation Stages

The number of theoretical stages in the steam stripping column required to achieve the desired separation of the more volatile constituents from the less volatile constituents is calculated from vapor-liquid equilibrium data, which are determined empirically. Using the theoretical number of stages, the actual number of stages can then be determined through the use of empirical tray efficiency data typically supplied by an equipment manufacturer. EPA examines the actual number of stages in the steam stripping column to ensure that the system is designed to achieve an effective degree of separation of organics from the wastewater.

### 9.5.2 Liquid and Vapor Flow Rates

The vapor-liquid equilibrium data are also used to determine the liquid and vapor flow rates that provide sufficient contact between the liquid and vapor streams. These rates are affected by the column diameter. EPA monitors the liquid and vapor flow rates to ensure that sufficient contact time between the liquid and vapor streams is provided to effectively separate the organics from the wastewater.

### 9.5.3 Stripping Temperature and Pressure

These parameters are integrally related to the vapor-liquid equilibrium conditions. The temperature at any point in the stripping column is an indicator of the constituent concentrations at that point, thus revealing whether the separation of components is taking place as expected. Overall column pressure influences the boiling point of the liquid at any location in the column. For example, through application of a partial vacuum to the column, the temperatures required to achieve the desired separation can be reduced because liquids volatilize at lower temperatures at reduced pressures. EPA monitors the temperature and pressure of a steam stripping column continuously, if possible, to ensure that the system is operating at the appropriate design conditions and to diagnose operational problems.

### 9.5.4 Internal Column Design

Column internals are designed to accommodate the physical and chemical properties of the wastewater to be stripped. Two types of internals may be used in steam stripping: trays or packing. Tray types include bubble cap, sieve, valve, and turbo-grid. Trays have several advantages over packing. They are less susceptible to blockage by solids, they have a lower capital cost for large-diameter columns (greater than approximately 3 feet), and they accommodate a wider range of liquid and vapor flow rates. Compared to trays, packing has the advantages of having a lower pressure drop per theoretical stage, being more resistant to corrosive materials, having a lower capital cost for small-diameter columns (less than approximately 3 feet), and being less susceptible to foaming because of a more uniform flow distribution (i.e., lower local variations in flow rates). EPA examines the internal column design of a steam stripping column to ensure that the system is designed to handle potential operational problems (e.g., corrosion, foaming, channeling, etc.).

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# 10. THIN FILM EVAPORATION

## 10.1 Applicability

Thin film evaporation is a form of distillation applicable to the treatment of wastes containing organics that are volatile enough to be removed by the application of heat. This technology can be used to treat highly concentrated organic wastes. However, the feed stream to a thin film evaporator must contain low concentrations of suspended solids. Use of this technology results in an organic product stream, which may be reused or further treated, and a bottoms stream, which is often incinerated.

## 10.2 Underlying Principles of Operation

As with other forms of distillation, the basic principle of operation for thin film evaporation is the separation of a liquid mixture into various components by a process of vaporization-condensation. The constituents that are volatilized are then condensed and either reused or further treated by liquid injection incineration. The constituents that are not volatilized may also be reused or incinerated as applicable.

An integral part of the theory of thin film evaporation is the principle of vapor-liquid equilibrium. When a liquid mixture of two or more components is heated, the vapor phase present above the liquid phase becomes more concentrated in the more volatile constituents (those having the higher vapor pressures). The vapor phase above the liquid phase is then cooled to yield a condensate that is also more concentrated in the more volatile components. The remaining liquid phase is richer in the less volatile components. The degree of separation of components depends on the relative differences in the vapor pressures of the constituents; the larger the difference in the vapor pressures, the more easily the separation can be accomplished.

If the difference between the vapor pressures is extremely large, a single separation cycle or a single equilibrium stage of vaporization and condensation may achieve a significant separation of the constituents. Typically, thin film units contain only one equilibrium stage and are thus limited in the degree of separation by the relative volatilities of the constituents. The greater the difference in component volatilities, the more likely it is that thin film evaporation will be effective.

The vapor-liquid equilibrium of the waste components can be expressed as relative volatility, which is the ratio of the vapor-to-liquid concentrations of a constituent divided by the ratio of the vapor-to-liquid concentrations of another constituent. The relative volatility is a direct measure of the ease of separation. If the numerical value is 1, then separation using thin film evaporation is impossible because the constituents have the same concentrations in the vapor and liquid phases. When the relative volatility is 1, the liquid mixture is called an azeotrope. Separation becomes easier as the value of the relative volatility becomes increasingly different from unity.

## 10.3 Description of Thin Film Evaporation Process

Typically, thin film evaporation consists of a steam-jacketed cylindrical vessel and a condenser. Figure 10-1 is a schematic showing the major components of a thin film evaporator. The steam-heated surface of the cylindrical vessel provides the heat required to vaporize the volatile constituents in the waste. The evaporator walls are heated from the outside as the feed trickles down the inside walls in a thin film. Unique to this form of distillation is the distribution device that spreads the thin film over the heated surface. The feed rate of waste is controlled to allow the more volatile material adequate time to vaporize. The heat transfer from the heating medium (steam) to the waste is determined by their relative temperatures, the heat transfer rate of

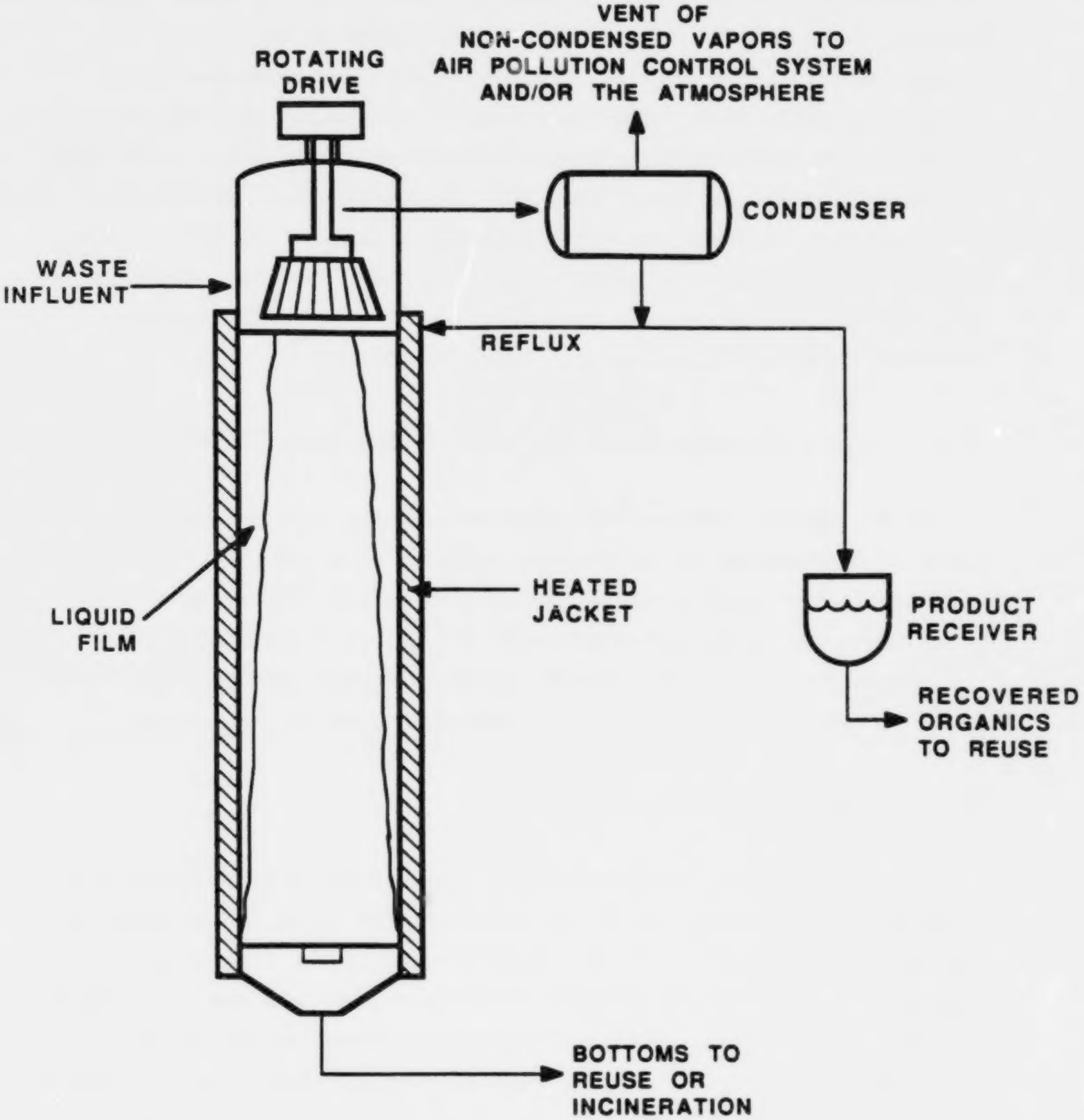
VENT OF NON-CONDENSED VAPORS TO AIR POLLUTION CONTROL SYSTEM AND/OR THE ATMOSPHERE
ROTATING DRIVE
CONDENSER
WASTE INFLUENT
REFLUX
LIQUID FILM
HEATED JACKET
PRODUCT RECEIVER
RECOVERED ORGANICS TO REUSE
BOTTOMS TO REUSE OR INCINERATION

**Figure 10-1. Thin Film Evaporation System.**

the vessel materials, and the thermal properties of the waste stream forming the film. The rising vapor is collected at the top of the column, cooled, and condensed in a condenser. The condensed liquid product stream is then routed to a product receiver. The "bottoms," which are the least volatile components of the waste, are continuously withdrawn from the bottom of the thin film evaporator. Because thin film evaporation is used to remove the volatile organics from wastes, the bottoms are reduced in volatile organic content. However, the bottoms generally require additional treatment, such as incineration for residual, less volatile organics, prior to disposal.

## 10.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether thin film evaporation will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the component boiling points, (b) the concentration of suspended solids, (c) the concentration of volatile components, and (d) the concentration of oil and grease.

### 10.4.1 Component Boiling Points

As noted earlier, the greater the ratio of volatility of the waste constituents, the more easily the separation of these constituents can proceed. This ratio is called relative volatility. EPA recognizes, however, that the relative volatilities cannot be measured or calculated directly for the types of wastes generally treated by thin film evaporation. This is because the wastes usually consist of a myriad of components, all with different vapor pressure-versus-temperature relationships. However, because the volatility of components is usually inversely proportional to their boiling points (i.e., the higher the boiling point, the lower the volatility), EPA uses the boiling point of waste components as a surrogate for relative volatility. If the differences in boiling points between the more volatile and less volatile constituents are lower in the untested waste than in the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 10.4.2 Concentration of Suspended Solids

Wastes containing large amounts of suspended solids, organic or inorganic, may coat heat transfer surfaces, thereby disturbing the uniform film and inhibiting volatilization of constituents. If the concentration of suspended solids in the untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance. Filtration may be required prior to thin film evaporation to reduce the concentration of suspended solids and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 10.4.3 Concentration of Volatile Components

The concentration of volatile components is a measure of the maximum fraction of the waste that can be expected to volatilize in the thin film evaporator. A relatively low concentration of volatile components implies that most of the waste may become bottoms (i.e., is nonvolatile). If the concentration of volatile components in the untested waste is significantly lower than that in the tested waste, the system may not achieve the same performance. Higher temperatures may be required to volatilize less volatile compounds and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 10.4.4 Concentration of Oil and Grease

High concentrations of oil and grease in the waste may result in coating of the evaporator walls, preventing a uniform film from forming and inhibiting volatilization of waste components. If the concentration of oil and grease in the untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 10.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a thin film evaporation system, EPA examines the following parameters: (a) the evaporator surface area, (b) the evaporation temperature and pressure, and (c) the waste feed rate.

### 10.5.1 Evaporator Surface Area

The evaporator surface area required to achieve the desired volatilization of organic components from the waste is calculated from the vapor-liquid equilibrium data, which are determined empirically, and from waste liquid flow rates. EPA examines the surface area of the evaporator to ensure that sufficient surface area is provided to achieve effective volatilization of the more volatile organic components.

### 10.5.2 Evaporation Temperature and Pressure

These parameters are integrally related to the vapor-liquid equilibrium conditions. To achieve the desired volatilization, the temperature of the evaporator must be maintained high enough to volatilize the volatile components from the waste at the waste flow rate. If the evaporator is operated at pressures below atmospheric (slight vacuum), lower temperatures can be used, requiring less heat input, because boiling points decrease as pressures decrease. EPA monitors the thin film evaporator temperature as well as the pressure (if pressures other than atmospheric are used) continuously, if possible, to ensure that the system is operating at the appropriate design conditions and to diagnose operational problems.

### 10.5.3 **Waste Feed Rate.**

The residence time is determined by the energy input into the system as well as the volatility of the components and the degree of purity desired. It is dependent on the distillation temperature and the boiling points of waste components. EPA monitors the waste feed rate continuously to ensure that sufficient residence time is provided to effectively volatilize organic components from the waste.

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# 11. ACID LEACHING

## 11.1 Applicability

Acid leaching is a treatment technology used to treat wastes in solid or slurry form containing metal constituents that are soluble in a strong acid solution or can be converted by reaction with a strong acid to a soluble form. This process has been used to recover metals such as copper, nickel, silver, and cadmium from inorganic wastes generated in the primary metals and inorganic chemicals industries.

The acid leaching process is most effective with wastes having high (over 1,000 ppm) levels of metal constituents. Wastes containing lower levels of such contaminants are more difficult to process because the low metal concentrations require longer contact times.

## 11.2 Underlying Principles of Operation

The basic principle of operation for acid leaching is that solubilities of various metals in acid solutions aids in their removal from a waste. The process concentrates the constituent(s) leached by the acid solutions. These constituents can then be filtered to remove residual solids and neutralized to precipitate solids containing high concentrations of the constituents of interest, which can be further treated in metals recovery processes. Alternatively, the acid solutions can be electrolyzed to recover pure metals. An acid leaching system usually consists of a solid/liquid contacting unit followed by a solid/liquid separator. The most frequently used acids include sulfuric ($H_2SO_4$), hydrochloric (HCl), and nitric ($HNO_3$). Although any acidic pH can theoretically be used, acid leaching processes are normally run at a pH from 1 to 4.

## 11.3 Description of Acid Leaching Process

Acid leaching processes can be categorized into two major types: (a) treatment by percolation of the acid through the solids or (b) treatment by dispersion of the solids within the acid solution. Both treatments are followed by subsequent separation of the solids from the liquid. In both types of systems, sufficient acid must be supplied to keep the pH at the level needed to effectively leach the metals from the waste.

### 11.3.1 Percolation Processes

Percolation is typically conducted in batch tanks. Batch percolators are large tanks ranging in size up to 50,000 gallons. First, the solids are placed in the tank, and then acid is added. The acid percolates through the solids and drains out through screens or a porous medium in the tank bottom. Following treatment, the solids are removed and further treated using stabilization and/or land disposed.

### 11.3.2 Dispersed-Solids Processes

Acid leaching by dispersion of fine solids into the acid is performed in batch tanks. The untreated waste and the acid are mixed in the reaction tank to ensure effective contact between the solids and the acid. Following mixing, the suspension may be pumped to stirred holding tanks, where the leaching is allowed to proceed to completion. The treated solids are then usually separated from the acid by filtration and further treated using stabilization and/or land disposed.

## 11.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether acid leaching will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the solid waste particle size, (b) the alkalinity of the waste, (c) the solubility of metal constituents in the acid, and (d) the concentration of leachable metals.

### 11.4.1 Solid Waste Particle Size

Both the solubility reaction rate of the acid with the hazardous metal constituents in the waste and the rate of transport of acid to and from the site of the hazardous constituents are affected by the size of the solid waste particles. The smaller the particles, the more rapidly they will leach because of the increased surface area of the waste that is exposed to the acid. If the particle size of the untested waste is greater than that for the tested waste, the system may not achieve the same performance. Grinding the untested waste may be required to reduce the particle size and achieve the same treatment performance, or it may be necessary to consider other, more applicable treatment technologies for treatment of the untested waste.

### 11.4.2 Alkalinity of the Waste

The neutralizing capacity (or alkalinity) of the waste solids affects the amount of acid that must be added to the waste in order to achieve and/or maintain the desired reactor pH. In addition to dissolving the waste contaminants, the acid will also dissolve some of the alkaline bulk solids; therefore, highly alkaline wastes require more acid or a stronger acid to maintain pH during treatment. If the alkalinity in an untested waste is greater than that in a tested waste, the system may not achieve the same performance. Use of additional acid or a stronger acid may be required to compensate for the increased alkalinity and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 11.4.3 Solubility of the Metal Constituents in the Acid

The metal constituents must dissolve in the acid to form soluble salts for the process to be effective. Thus, the acid selected should be one that forms soluble salts for all of the constituents to be removed. If the solubility of a certain metal constituent(s) of concern in an untested waste is less than that of another constituent(s) of concern in a previously tested waste in the same acid, or less than the solubility of the same metal(s) tested with a different acid, the system may not achieve the same performance. Use of another acid may be required to increase the solubilities of the metal constituent(s) of concern and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 11.4.4 Concentration of Leachable Metals

The amount of leachable metals is a measure of the maximum fraction of the waste that can be expected to leach in the acid leaching system. A relatively low concentration of leachable metals implies that most of the waste will remain in the solid or slurry waste residues (i.e., nonleachable). If the concentration of leachable metals in the untested waste is significantly less than that in the tested waste, the system may not achieve the same performance. Use of a higher concentration of acid or a stronger acid may be required to leach less-leachable components and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 11.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of an acid leaching system, EPA examines the following parameters: (a) the residence time, (b) the type and concentration of acid used, (c) the pH, and (d) the degree of mixing.

### 11.5.1 Residence Time

The extent of reaction and dissolution of the contaminants in the acid is directly related to the contact time. EPA monitors the residence time to ensure that sufficient time is provided to effectively leach the metal contaminants from the waste.

### 11.5.2 Type and Concentration of Acid Used

If the hazardous constituents to be removed in the acid leaching system are already present in the waste in soluble form, or are solubilized by pH reduction, then any acid that will reduce the pH to the desired value may be used. However, if chemical reaction is necessary to form soluble species, then the appropriate acid, as well as the appropriate concentration of the acid, must be used to ensure effective leaching of the metal constituents. EPA examines the type and concentration of acid used to ensure that the acid solution selected is capable of effectively leaching the metal constituents from the waste.

### 11.5.3 pH

For dispersed solids systems, the feed of acid to the leaching reactor is based on pH monitoring and control because the reaction rate is highly pH dependent. Therefore, a pH should be determined, based on the residence time and amount of hazardous metal constituents in the waste, that provides for complete dissolution of metal constituents. For percolation systems, pH monitoring of the acid percolating through the tank (i.e., leaving the system) should ensure that enough acid is being added. EPA monitors the pH to ensure that the system is operating at the appropriate design conditions and to diagnose operational problems.

### 11.5.4 Degree of Mixing

Mixing provides greater contact between the acid and the solid waste particles, ensuring more rapid leaching of metal contaminants from the waste. The quantifiable degree of mixing is a complex assessment that includes, among other things, the amount of energy supplied, the length of time the material is mixed, and the related turbulence effects of the specific size and shape of the tank. This is beyond simple measurement. EPA, however, evaluates the degree of mixing qualitatively by considering whether mixing is provided and whether the type of mixing device is one that could be expected to achieve uniform mixing of the waste solution.

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# 12. CHEMICAL PRECIPITATION

## 12.1 Applicability

Chemical precipitation is a treatment technology applicable to wastewaters containing a wide range of dissolved and other metals, as well as other inorganic substances such as fluorides. This technology removes these metals and inorganics from solution in the form of insoluble solid precipitates. The solids formed are then separated from the wastewater by settling, clarification, and/or polishing filtration.

For some wastewaters, such as chromium plating baths or plating baths containing cyanides, the metals exist in solution in a very soluble form. This solubility can be caused by the metal's oxidation state (for hexavalent chromium wastewaters) or by complexing of the metals (for high cyanide-containing wastewaters). In both cases, pretreatment, such as hexavalent chromium reduction or oxidation of the metal-cyanide complexes, may be required before the chemical precipitation process can be applied effectively.

## 12.2 Underlying Principles of Operation

The basic principle of operation of chemical precipitation is that metals and inorganics in wastewater are removed by the addition of a precipitating agent that converts the soluble metals and inorganics to insoluble precipitates. These precipitates are settled, clarified, and/or filtered out of solution, leaving a lower concentration of metals and inorganics in the wastewater. The principal precipitation agents used to convert soluble metal and inorganic compounds to less soluble forms include: lime ($Ca(OH)_2$), caustic ($NaOH$), sodium sulfide ($Na_2S$), and, to a lesser extent, soda ash ($Na_2CO_3$), phosphate ($PO_4^{-}$), and ferrous sulfide ($FeS$).

The solubility of a particular compound depends on the extent to which the electrostatic forces holding the ions of the compound together can be overcome. The solubility changes significantly with temperature, with most metal compounds becoming more soluble as the temperature increases. Additionally, the solubility is affected by other constituents present in the wastewater, including other ions and complexing agents. Regarding specific ionic forms, nitrates, chlorides, and sulfates are, in general, more soluble than hydroxides, sulfides, carbonates, and phosphates.

Once the soluble metal and inorganic compounds have been converted to precipitates, the effectiveness of chemical precipitation is determined by how successfully they are physically removed. Removal usually relies on a settling process; that is, a practicle of a specific size, shape, and composition will settle at a specific velocity, as described by Stokes' Law. For a batch system, Stokes' Law is a good predictor of settling time because the pertinent particle parameters essentially remain constant. In practice, however, settling time for a batch system is normally determined by empirical testing. For a continuous system, the theory of settling is complicated by such factors as turbulence, short-circuiting of the wastewater, and velocity gradients, which increases the importance of empirical tests to accurately determine appropriate settling times.

## 12.3 Description of Chemical Precipitation Process

The equipment and instrumentation required for chemical precipitation vary depending on whether the system is batch or continuous. Both systems are discussed below.

For a batch system, chemical precipitation requires a feed system for the treatment chemicals and a reaction tank where the waste can be treated and allowed to settle. When lime is used, it is usually added to the reaction tank in a slurry form. The supernatant liquid is generally analyzed before discharge to ensure that settling of precipitates is adequate.

For a continuous system, additional tanks are necessary, as well as the instrumentation to ensure that the system is operating properly. A schematic of a continuous chemical precipitation system is shown in Figure 12-1. In this system, wastewater is fed into an equalization tank where it is mixed to provide more uniformity, thus minimizing the variability in the type and concentration of constituents sent to the reaction tank.

Following equalization, the wastewater is pumped to a reaction tank where precipitating agents are added. This is done automatically by using instrumentation that senses the pH of the system for hydroxide precipitating agents, or the oxidation-reduction potential (ORP) for non-hydroxide precipitating agents, and then pneumatically adjusts the position of the treatment chemical feed valve until the design pH or ORP value is achieved. (The pH and ORP values are affected by the concentration of hydroxide and non-hydroxide precipitating agents, respectively, and are thus used as indicators of their concentrations in the reaction tank.)

In the reaction tank, the wastewater and precipitating agents are mixed to ensure commingling of the metal and inorganic constituents to be removed and the precipitating agents. In addition, effective dispersion of the precipitating agents throughout the tank is necessary to properly monitor and thereby control the amount added.

Following reaction of the wastewater with the stabilizing agents, coagulating or flocculating compounds are added to chemically assist the settling process. Coagulants and flocculants increase the particle size

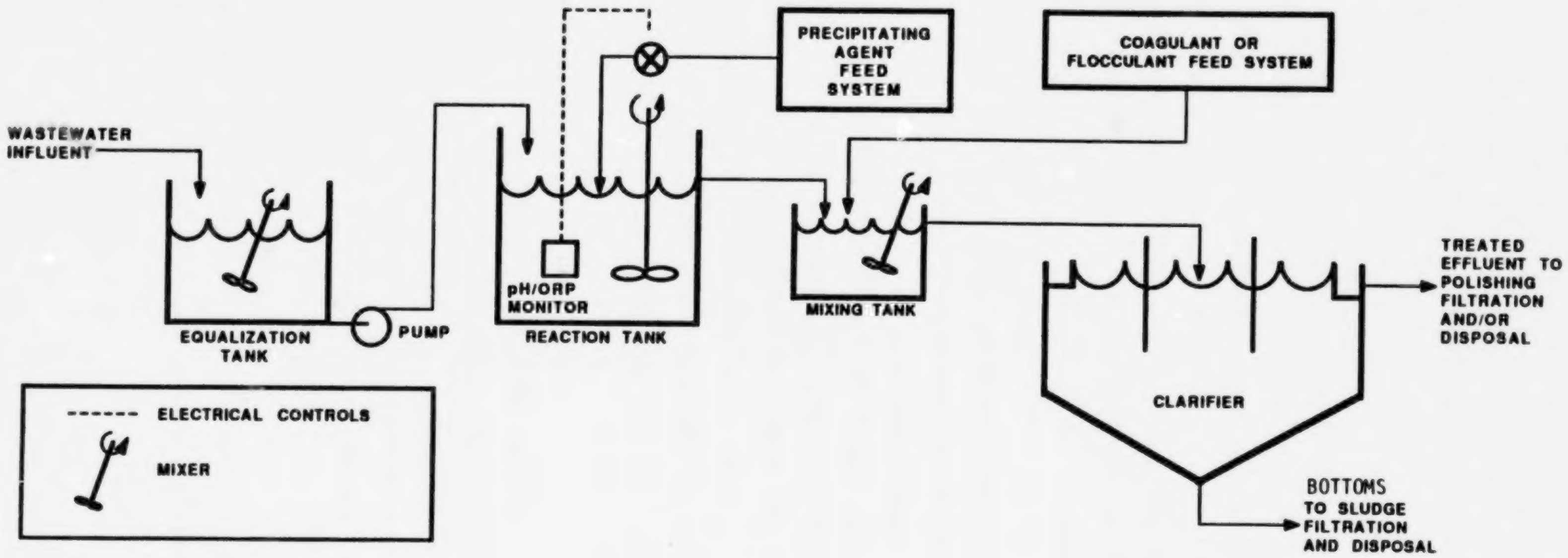

WASTEWATER INFLUENT
EQUALIZATION TANK
PUMP
pH/ORP MONITOR
REACTION TANK
PRECIPITATING AGENT FEED SYSTEM
COAGULANT OR FLOCCULANT FEED SYSTEM
MIXING TANK
CLARIFIER
TREATED EFFLUENT TO POLISHING FILTRATION AND/OR DISPOSAL
BOTTOMS TO SLUDGE FILTRATION AND DISPOSAL
------ ELECTRICAL CONTROLS
MIXER

Figure 12-1. Continuous Chemical Precipitation System.

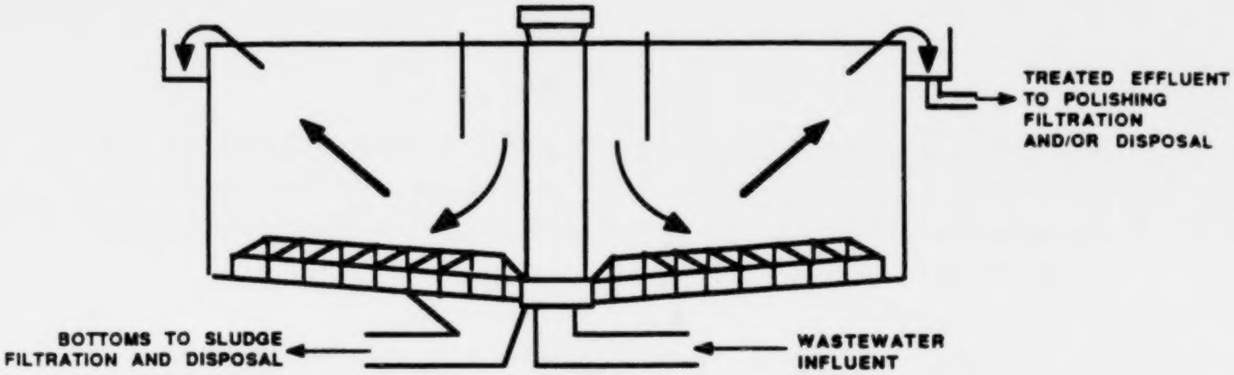
and density of the precipitated solids, both of which increase the rate of settling. The coagulant or flocculating agent that best improves settling characteristics varies depending on the particular precipitates to be settled.

Settling can be conducted in a large tank by relying solely on gravity or can be mechanically assisted through the use of a circular clarifier or an inclined plate settler. Schematics of the two settling systems are shown in Figures 12-2 and 12-3. Following the addition of coagulating or flocculating agents, the wastewater is fed to a large settling tank, circular clarifier, or inclined plate settler where the precipitated solids are removed. These solids are generally further treated in a sludge filtration system to dewater them prior to disposal. This technology is discussed in Section 21 of this report.

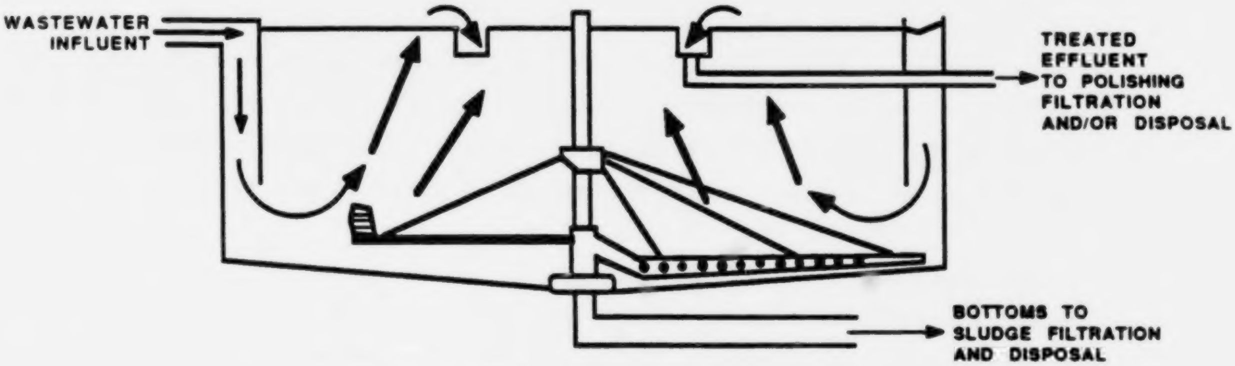
The supernatant liquid effluent can be further treated in a polishing filtration system to remove precipitated residuals both in cases where the settling system is underdesigned and in cases where the particles are difficult to settle. Polishing filtration is discussed in Section 20 of this report.

## 12.4 Waste Characteristics Affecting Performance (WCAPs)

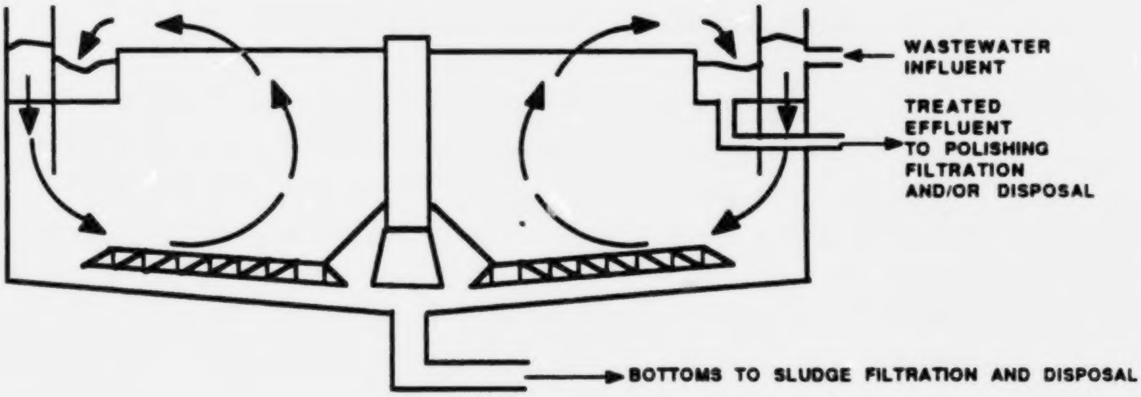
In determining whether chemical precipitation will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the concentration and type of metals, (b) the concentration of total dissolved solids (TDS), (c) the concentration of complexing agents, and (d) the concentration of oil and grease.


TREATED EFFLUENT TO POLISHING FILTRATION AND/OR DISPOSAL
BOTTOMS TO SLUDGE FILTRATION AND DISPOSAL
WASTEWATER INFLUENT

CENTER FEED CLARIFIER WITH SCRAPER SLUDGE REMOVAL SUSTEM


WASTEWATER INFLUENT
TREATED EFFLUENT TO POLISHING FILTRATION AND/OR DISPOSAL
BOTTOMS TO SLUDGE FILTRATION AND DISPOSAL

RIM FEED - CENTER TAKEOFF CLARIFIER WITH
HYDRAULIC SUCTION SLUDGE REMOVAL SYSTEM


WASTEWATER INFLUENT
TREATED EFFLUENT TO POLISHING FILTRATION AND/OR DISPOSAL
BOTTOMS TO SLUDGE FILTRATION AND DISPOSAL

RIM FEED - RIM TAKEOFF CLARIFIER

Figure 12-2. Circular Clarifier Systems.

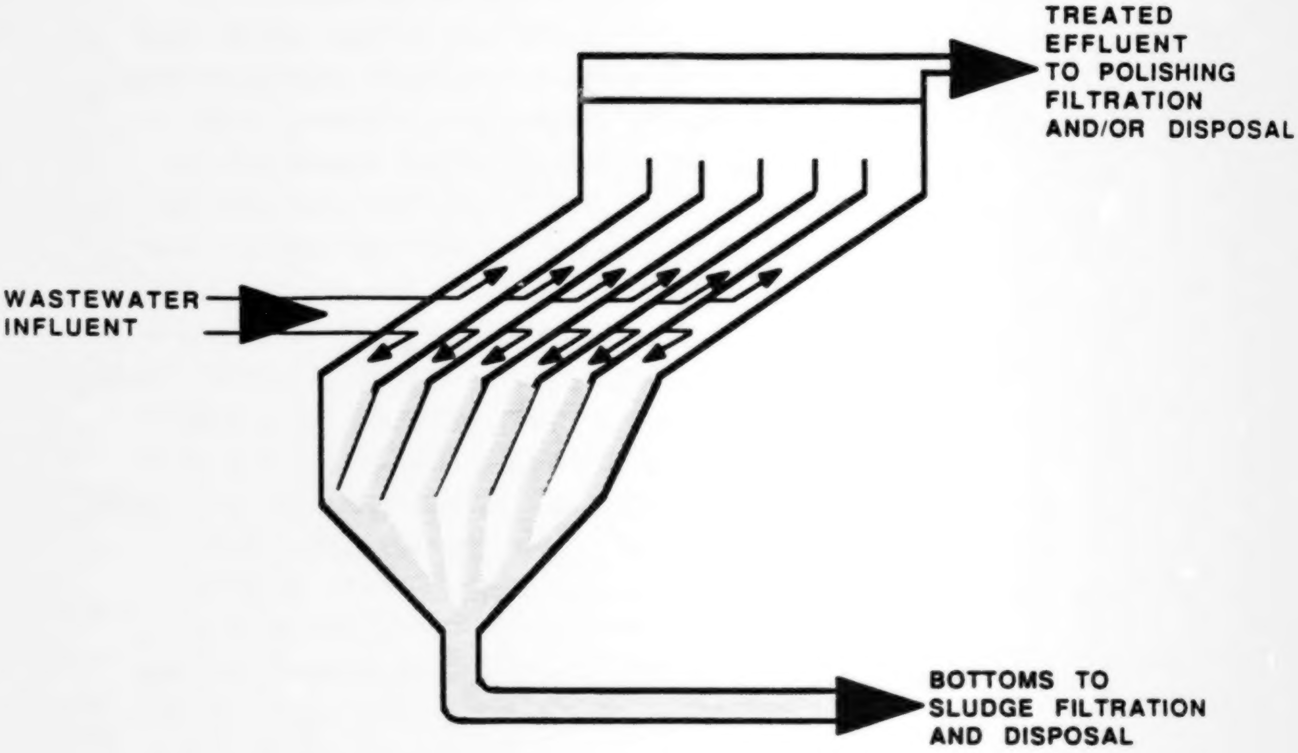

TREATED EFFLUENT TO POLISHING FILTRATION AND/OR DISPOSAL
WASTEWATER INFLUENT
BOTTOMS TO SLUDGE FILTRATION AND DISPOSAL

Figure 12-3. Inclined Plate Settler System.

### 12.4.1 Concentration and Type of Metals

For most metals, there is a specific pH at which the metal precipitate is least soluble. As a result, when a waste contains a mixture of many metals, it is not possible to operate a treatment system at a single pH or ORP value that is optimal for the removal of all metals. The extent to which this affects treatment depends on the particular metals to be removed and their respective concentrations. One alternative is to operate multiple precipitations, with intermediate settling, when the optimum pH occurs at markedly different levels for the metals present. If the concentration and type of metals in an untested waste differ from and are significantly higher than those in the tested waste, the system may not achieve the same performance. Additional precipitating agents, alternate pH/ORP values, and/or multiple precipitations may be required to achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 12.4.2 Concentration of Total Dissolved Solids (TDS)

High concentrations of total dissolved solids can interfere with precipitation reactions, as well as inhibit settling. Poor precipitate formation and flocculation are results of high TDS concentrations, and higher concentrations of solids are found in the treated wastewater residuals. If the TDS concentration in an untested waste is significantly higher than in the tested waste, the system may not achieve the same performance. Higher concentrations of precipitating agents may be required to achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 12.4.3 Concentration of Complexing Agents

Metal complexes consist of a metal ion surrounded by a group of other inorganic or organic ions or molecules (often called ligands). In the complexed form, metals have a greater solubility. Also, complexed metals inhibit the reaction of the metal with the precipitating agents and therefore may not be removed as effectively from solution by chemical precipitation. However, EPA does not have analytical methods to determine the concentration of complexed metals in wastewaters. The Agency believes that the best indicator for complexed metals is to analyze for complexing agents, such as cyanide, chlorides, EDTA, ammonia, amines, and methanol, for which analytical methods are available. Therefore, EPA uses the concentration of complexing agents as a surrogate waste characteristic for the concentration of metal complexes. If the concentration of complexing agents in an untested waste is significantly higher than in the tested waste, the system may not achieve the same performance. Higher concentrations of precipitating agents may be required to achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 12.4.4 Concentration of Oil and Grease

The concentration of oil and grease in a waste inhibits the settling of the precipitate by creating emulsions that require a long settling time. Suspended oil droplets in water tend to suspend particles such as chemical precipitates that would otherwise settle out of solution. Even with the use of coagulants or flocculants, the settling of the precipitate is less effective. If the concentration of oil and grease in an untested waste is significantly higher than in the tested waste, the system may not achieve the same performance. Pretreatment of the waste may be required to reduce the oil and grease concentration and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 12.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a chemical precipitation system, EPA examines the following parameters: (a) the pH/ORP value; (b) the precipitation temperature; (c) the residence time; (d) the amount and type of precipitating agents, coagulants, and flocculants; (e) the degree of mixing; and (f) the settling time.

### 12.5.1 pH/ORP Value

The pH/ORP value in continuous chemical precipitation systems is used as an indicator of the concentration of precipitating agents in the reaction tank and, thus, to regulate their addition to the tank. The pH/ORP value also affects the solubility of metal precipitates formed and therefore directly impacts the effectiveness of their removal. EPA monitors the pH/ORP value continuously, if possible, to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

### 12.5.2 Precipitation Temperature

The precipitation temperature affects the solubility of the metal precipitates. Generally, the lower the temperature, the lower the solubility of the metal precipitates and vice versa. EPA monitors the precipitation temperature continuously, if possible, to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

### 12.5.3 Residence Time

The residence time impacts the extent of the chemical reactions to form metal precipitates and, as a result, the amount of precipitates that can be settled out of solution. For batch systems, the residence time is controlled directly by adjusting the treatment time in the reaction tank. For continuous systems, the wastewater feed rate is controlled to make sure that the system is operating at the appropriate design residence time. EPA monitors the residence time to ensure that sufficient time is provided to effectively precipitate from the wastewater.

### 12.5.4 Amount and Type of Precipitating Agents, Coagulants, and Flocculants

The amount and type of precipitating agent used to effectively treat the wastewater depends on the amount and type of metal and inorganic constituents in the wastewater to be treated. Other design and operating parameters, such as the pH/ORP value, the precipitation temperature, the residence time, the amount and type of coagulants and flocculants, and the settling time, are determined by the selection of precipitating agents.

The addition of coagulants and flocculants improves the settling rate of the precipitated metals and inorganics and allows for smaller settling systems (i.e., lower settling time) to achieve the same degree of settling as a much larger system. Typically, anionic polyelectrolyte flocculating agents are most effective with metal precipitates, although cationic or non-ionic polyelectrolytes also are effective. Typical doses range from 0.1 to 10 mg/l of the total influent wastewater stream. Conventional coagulants, such as alum (aluminum sulfate), are also effective, but must be dosed at much higher concentrations to achieve the same result. Therefore, these coagulants add more to the settled sludge volume requiring disposal than do the polyelectrolyte flocculants. EPA examines the amount and type of precipitating agents, coagulants, and flocculants added, and their method of addition to the wastewater, to ensure effective precipitation.

### 12.5.5 Degree of Mixing

Mixing provides greater uniformity of the wastewater feed and disperses precipitating agents, coagulants, and flocculants throughout the wastewater to ensure the most rapid precipitation reactions and settling of precipitate solids possible. The quantifiable degree of mixing is a complex assessment that includes, among other things, the amount of energy supplied, the length of time the material is mixed, and the related turbulence effects of the specific size and shape of the tank. This is beyond the scope of simple measurement. EPA, however, evaluates the degree of mixing qualitatively by considering whether mixing is provided and whether the type of mixing device is one that could be expected to achieve uniform mixing of the wastewater.

### 12.5.6 Settling Time

Adequate settling time must be provided to make sure that removal of the precipitated solids from the wastewater has been completed. EPA monitors the settling time to ensure effective solids removal.

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# 13. ELECTROLYTIC OXIDATION OF CYANIDE

## 13.1 Applicability

Electrolytic oxidation is a treatment technology applicable to wastes containing high concentrations of cyanide in solution. Because of excessive retention time requirements, the process is often applied as preliminary treatment for highly concentrated cyanide wastes, prior to more conventional chemical cyanide oxidation (Cushnie 1985).

This treatment technology is used in industry for the destruction of cyanide in (a) concentrated spent plating solutions and stripping solutions, (b) spent heat treating baths, (c) alkaline descalers, and (d) metal passivating (rust-inhibiting) solutions. Electrolytic oxidation has been demonstrated successfully for treatment of wastes containing concentrations of cyanide up to 100,000 mg/l (Easton 1967). However, for concentrations of cyanide lower than 500 mg/l, chemical oxidation treatment may be more efficient.

## 13.2 Underlying Principles of Operation

The basic principle of operation for electrolytic oxidation of cyanide is that concentrated cyanide waste subject to an electrolytic reaction with dissolved oxygen in an aqueous solution is broken down to the gaseous products carbon dioxide ($CO_2$), nitrogen ($N_2$), and ammonia ($NH_3$). The process is conducted at elevated temperatures for periods ranging from several hours to over a week, depending on the initial cyanide concentration and the desired final cyanide concentration. The theoretical destruction process that takes place at the anodes is described by the following reaction:

$$\underset{\text{cyanide ion}}{2CN^-} + \underset{\text{oxygen}}{2O_2} \xrightarrow{\text{Electricity}} \underset{\text{carbon dioxide}}{2CO_2} + \underset{\text{nitrogen}}{N_2} + \underset{\text{electrons}}{2e^-}$$

The effectiveness of electrolytic oxidation is dependent on the conductivity of the waste, which is a function of several waste characteristics including the concentration of cyanide and other ions in solution. As the process continues, the waste becomes less capable of conducting electricity as cyanide concentration is reduced, causing the electrolytic reaction to be much less efficient at longer retention times.

## 13.3 Description of Electrolytic Oxidation Process

Typically, electrolytic destruction of cyanide takes place in a closed cell. This cell consists of two electrodes suspended in an aqueous solution, with direct current (DC) electricity supplied to drive the reaction to completion. The temperature of the bath containing the cyanide waste is maintained at or above 52°C (125°F). Sodium chloride may be added to the solution as an electrolyte (conductor) to increase the conductivity of the waste being treated. Since the reaction may take days or weeks, water is usually added to the tank periodically to make up for losses due to evaporation from the heated tank. This is necessary to ensure that the electrodes remain fully submerged so that a full flow of current is maintained in the solution during treatment. Following treatment, the treated waste is generally further treated in a conventional chemical oxidation system to destroy residual cyanides.

## 13.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether electrolytic oxidation will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the concentration of other oxidizable materials and (b) the concentration of reducible metals.

### 13.4.1 Concentration of Other Oxidizable Materials

The presence of oxidizable organics (such as oil and grease and surfactants) and the presence of inorganic ionic species in a reduced state (such as trivalent chromium or sulfide) may increase the treatment time required to achieve destruction of cyanide because these materials may be oxidized preferentially to the cyanide in solution. If concentrations of other oxidizable materials are significantly higher in the untested waste than in the tested waste, the system may not achieve the same performance. Longer reaction time may be required to oxidize cyanide and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 13.4.2 Concentration of Reducible Metals

The electrolytic process may cause some of the more easily reduced metals in the waste, such as copper, to plate out onto the anode as the pure metal. The plating of metals onto the anode may result in changes in current density and, hence, may change the rate of cyanide oxidation. If the concentration of reducible metals in the untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 13.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of an electrolytic oxidation system, EPA examines the following parameters: (a) the oxidation temperature, (b) the residence time, (c) the pH, (d) the electrical conductivity, (e) the electrode spacing and surface area, and (f) the degree of mixing.

### 13.5.1 Oxidation Temperature

For the electrolytic process, elevated temperatures are used. Normal temperatures range from 52 to 93°C (125 to 200°F). The temperature can be raised by increasing the flow of steam to the coils or jacket supplying heat to the reactor contents. EPA monitors the oxidation temperature to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

### 13.5.2 Residence Time

Electrolytic oxidation is usually a batch process. The time allowed to complete the reaction is an important factor in electrolysis and is dependent on the initial concentration of the waste and the desired final cyanide concentration. The rate of cyanide destruction decreases as the cyanide concentration decreases (i.e., the rate of cyanide destruction asymptotically approaches zero). Typical residence times range from periods of several hours to more than a week. EPA observes the residence time to ensure that sufficient time is provided to effectively destroy the cyanides in the wastes.

### 13.5.3 pH

Typical solutions for electrolytic oxidation have a pH ranging from 11.5 to 12.0. The pH must be maintained in the alkaline range to prevent liberation of toxic hydrogen cyanide. Typically, pH is controlled by the addition of caustic or lime. EPA monitors the pH to ensure that the treatment system is operating at the appropriate design condition and to diagnose operational problems.

### 13.5.4 Electrical Conductivity

The solution must have a high enough electrical conductivity to allow the reaction to proceed at an acceptable rate. If the conductivity is not high enough, it can be improved by adding an electrolyte such as sodium chloride. The conductivity of the waste during the reaction is normally determined by monitoring both the current and voltage of the cell. EPA monitors the electrical conductivity to ensure that the treatment system is operating at the appropriate design condition.

### 13.5.5 Electrode Spacing and Surface Area

The spacing and surface area of the electrodes directly impact the current flowing through the waste. The reaction rate is increased by both closer electrode spacing and more electrode surface area because each increases the current density in the cell. EPA observes the electrode spacing and surface area to ensure that sufficient current density is provided to effectively destroy the cyanides in the waste.

### 13.5.6 Degree of Mixing

Electrolytic destruction of cyanide requires good mixing in the reaction vessel. Mixing helps ensure an adequate supply of oxygen (from the air) for the electrochemical reaction (see Section 13.2, Underlying Principles of Operation), enhances mass transfer to promote the oxidation reaction, and keeps suspended solids in suspension. Mixing may be provided by the bubbling of air from the bottom of the reactor, or an external source of mixing may be provided. The quantifiable degree of mixing is a complex assessment that includes, among other things, the amount of energy supplied, the length of time the material is mixed, and the related turbulence effects of the size and shape of the reaction vessel used. This is beyond the scope of simple measurement. EPA, however, evaluates the degree of mixing qualitatively by considering whether mixing is provided and whether the type of mixing device is one that could be expected to achieve uniform mixing of the waste.

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# 14. HEXAVALENT CHROMIUM REDUCTION

## 14.1 Applicability

Hexavalent chromium reduction is a treatment technology applicable to wastes containing hexavalent chromium wastes, including plating solutions, stainless steel acid baths and rinses, "chrome conversion" coating process rinses, and chromium pigment manufacturing wastes. Because this technology requires that the pH be in the acidic range, it would not be applicable to a waste that contains significant amounts of cyanide or sulfide. In such cases, lowering of the pH can result in the release of toxic gases such as hydrogen cyanide or hydrogen sulfide. It is important to note that additional precipitation treatment is required to remove trivalent chromium from the solution following reduction of the hexavalent chromium.

## 14.2 Underlying Principles of Operation

The basic principle of hexavalent chromium reduction is to reduce the valence of chromium in solution (in the form of chromate or dichromate ions) from the hexavalent state to the trivalent state. "Reducing agents" used to effect the reduction include sodium sulfite ($Na_2S_2O_3$), sodium bisulfite ($NaHSO_3$), sodium metabisulfite ($Na_2S_2O_5$), sulfur dioxide ($SO_2$), sodium hydrosulfide (NaHS), and the ferrous form of iron ($Fe^{+2}$).

A typical reduction reaction, using sodium sulfite as the reducing agent, is as follows:

$$H_2(Cr^{+6})_2O_7 + 3Na_2SO_3 + 3H_2SO_4 \rightarrow (Cr^{+3})_2(SO_4)_3 + 3Na_2SO_4 + 4H_2O$$

The reaction is usually accomplished at pH values from 2 to 3.

At the completion of the chromium reduction step, the trivalent chromium compounds are precipitated from solution by raising the pH above 8. The insoluble trivalent chromium (in the form of chromium hydroxide) is then allowed to settle from solution. The precipitation reaction is as follows:

$$Cr_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Cr(OH)_3 + 3CaSO_4$$

## 14.3 Description of Chromium Reduction Process

The chromium reduction treatment process can be operated in a batch or continuous mode. A batch system consists of a reaction tank, a mixer to homogenize the contents of the tank, a supply of reducing agent, and a source of acid and base for pH control.

A continuous chromium reduction treatment system, as shown in Figure 14-1, usually includes a holding tank upstream of the reaction tank for flow and concentration equalization. It also includes instrumentation to automatically control the amount of reducing agent added and the pH of the reaction tank. The amount of reducing agent is controlled by the use of a sensor called an oxidation reduction potential (ORP) cell. The ORP sensor electronically measures, in millivolts, the level to which the redox reaction has proceeded at any given time. It must be noted, however, that the ORP reading is very pH dependent. Consequently, if the pH is not maintained at a steady value, the ORP will vary somewhat, regardless of the level of chromate reduction. Following chromium reduction, the trivalent chromium is precipitated and settled out of the solution, which is further treated and/or disposed. Precipitated trivalent chromium is either reused or further treated by stabilization and land disposed.

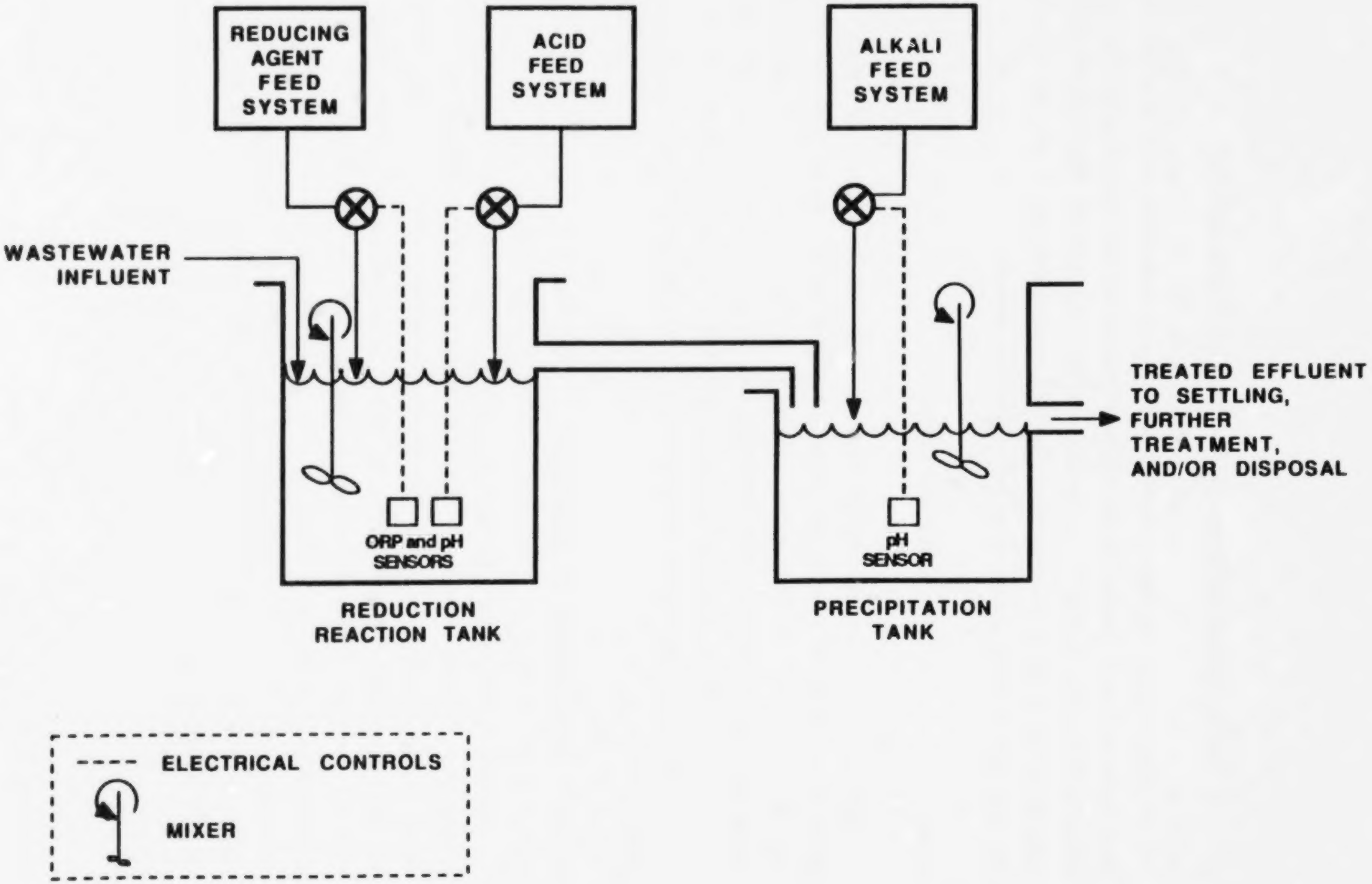
REDUCING AGENT FEED SYSTEM
ACID FEED SYSTEM
ALKALI FEED SYSTEM
WASTEWATER INFLUENT
ORP and pH SENSORS
pH SENSOR
TREATED EFFLUENT TO SETTLING, FURTHER TREATMENT, AND/OR DISPOSAL
REDUCTION REACTION TANK
PRECIPITATION TANK
ELECTRICAL CONTROLS
MIXER

Figure 14-1. Continuous Hexavalent Chromium Reduction System.

## 14.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether hexavalent chromium reduction will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the concentration of oil and grease and (b) the concentration of other reducible metals.

### 14.4.1 Concentration of Oil and Grease

EPA believes that oil and grease compounds could cause monitoring problems because of fouling of instrumentation (e.g., electrodes for pH and ORP sensors). If the concentration of oil and grease in the untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 14.4.2 Concentration of Other Reducible Metals

Ionized metals (such as silver, copper, and mercury) can compete with chromium for reducing agents, thereby requiring greater amounts of reducing agents to completely reduce the chromium. If the concentration of reducible metals in the untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance. Additional reducing agents may be required to reduce the chromium and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 14.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a hexavalent chromium reduction system, EPA examines the following parameters: (a) the amount and type of reducing agent, (b) the pH, (c) the residence time, and (d) the degree of mixing.

### 14.5.1 Amount and Type of Reducing Agent

The choice of a reducing agent establishes the chemical reaction upon which the chromium reduction system is based. The amount of reducing agent must be monitored and controlled in both batch and continuous systems to ensure complete reduction. In batch systems, reducing agent is usually controlled by analysis of the hexavalent chromium remaining in solution, but it may also be controlled by using an ORP monitoring system. For continuous systems, the ORP reading is used to monitor and control the addition of reducing agent.

The ORP will slowly change until the reduction reaction is completed at which point the ORP will change rapidly. The set point for the ORP monitor is approximately the reading just after the rapid change has begun. The reduction system must then be monitored periodically to determine whether the selected set point needs further adjustment. EPA monitors the hexavalent chromium remaining in solution for batch systems and monitors the ORP continuously, if possible, for continuous systems to ensure that an effective amount of the reducing agent has been added to the system.

### 14.5.2 pH

For batch and continuous systems, pH affects the reduction reaction. The reaction speed is significantly reduced at pH values above approximately 4.0. For a batch system, the pH can be monitored intermittently during treatment. For a continuous system, the pH must be continuously monitored because of its effect on the ORP reading. EPA monitors the pH to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

### 14.5.3 Residence Time

The residence time impacts the extent to which the hexavalent chromium reduction reaction goes to completion. For batch systems, the residence time is controlled directly by adjusting the treatment time in the reaction tank. For continuous systems, the feed rate is controlled to make sure that the system is operated at the appropriate design residence time. EPA monitors the residence time to ensure that sufficient time is provided to effectively reduce the waste.

### 14.5.4 Degree of Mixing

The reduction system should be designed to provide adequate mixing in order to ensure uniform distribution of the reducing agent and chromium throughout the reactor. The quantifiable degree of mixing is a complex assessment that includes, among other things, the amount of energy supplied, the length of time the material is mixed, and the related turbulence effects of the specific size and shape of the reaction vessel. This is beyond the scope of simple measurement. EPA, however, evaluates the degree of mixing qualitatively by considering whether mixing is provided and whether the type of mixing device is one that could be expected to achieve uniform mixing of the waste.

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# 15. HIGH TEMPERATURE METALS RECOVERY

## 15.1 Applicability

High temperature metals recovery (HTMR) is a technology applicable to wastes containing metal oxides and metal salts (including cadmium, chromium, lead, nickel, and zinc compounds) at concentrations ranging from 10 percent to over 70 percent with low levels (i.e., below 5 percent) of organics and water in the wastes. There are a number of different types of high temperature metals recovery systems, which generally differ from one another in the source of energy used and the method of recovery. These HTMR systems include the rotary kiln process, the plasma arc reactor, the rotary hearth electric furnace system, the molten slag reactor, and the flame reactor.

HTMR is generally not used for mercury-containing wastes even though mercury will volatilize readily at the process temperatures present in the high temperature units. The retorting process is normally used for mercury recovery because mercury is very volatile and lower operating temperatures can be used. Thus, the retorting process is more economical than HTMR for mercury-bearing wastes. Retorting is discussed in Section 7.

The HTMR process has been demonstrated on wastes such as baghouse dusts and dewatered scrubber sludge from the production of steels and ferroalloys. Zinc, cadmium, and lead are the metals most frequently recovered. The process has not been extensively evaluated for use with metal sulfides. The sulfides are chemically identical to natural minerals ordinarily present in ores used as feedstocks by primary smelters. Some sulfide-bearing wastes from the chrome pigments industry have been sent to such primary smelters. However, with sulfides, a possibility exists for formation of either carbon disulfide from reaction with carbon or sulfur dioxide from reaction with oxygen in the HTMR processes.

Metal halide salts are also not directly used in HTMR processes. They, however, may be converted to oxides or hydroxides, which are acceptable feedstocks for HTMR processes.

## 15.2 Underlying Principles of Operation

The basic principle of operation for HTMR is that metal oxides and salts are separated from a waste through a high temperature thermal reduction process that uses carbon, limestone, and silica (sand) as raw materials. The carbon acts as a reducing agent and reacts with metal oxides to generate carbon dioxide and free metal. The silica and limestone serve as fluxing agents. This process yields a metal product for reuse and reduces the concentration of metals in the residuals and, hence, the amount of waste that needs to be land disposed. An example HTMR reaction is the recovery of zinc, which proceeds as follows:

$$2\ ZnO + C \rightarrow 2\ Zn + CO_2$$

## 15.3 Description of High Temperature Metals Recovery Process

The HTMR process consists of a mixing unit, a high temperature processing unit (kiln, furnace, etc.), a product collection system, and a residual treatment system. A schematic diagram for a high temperature metals recovery system is shown in Figure 15-1.

The mixing unit homogenizes metal-bearing wastes, thus minimizing feed variations to the high temperature processing unit. Before the wastes are fed into the high temperature processing unit, fluxing agents

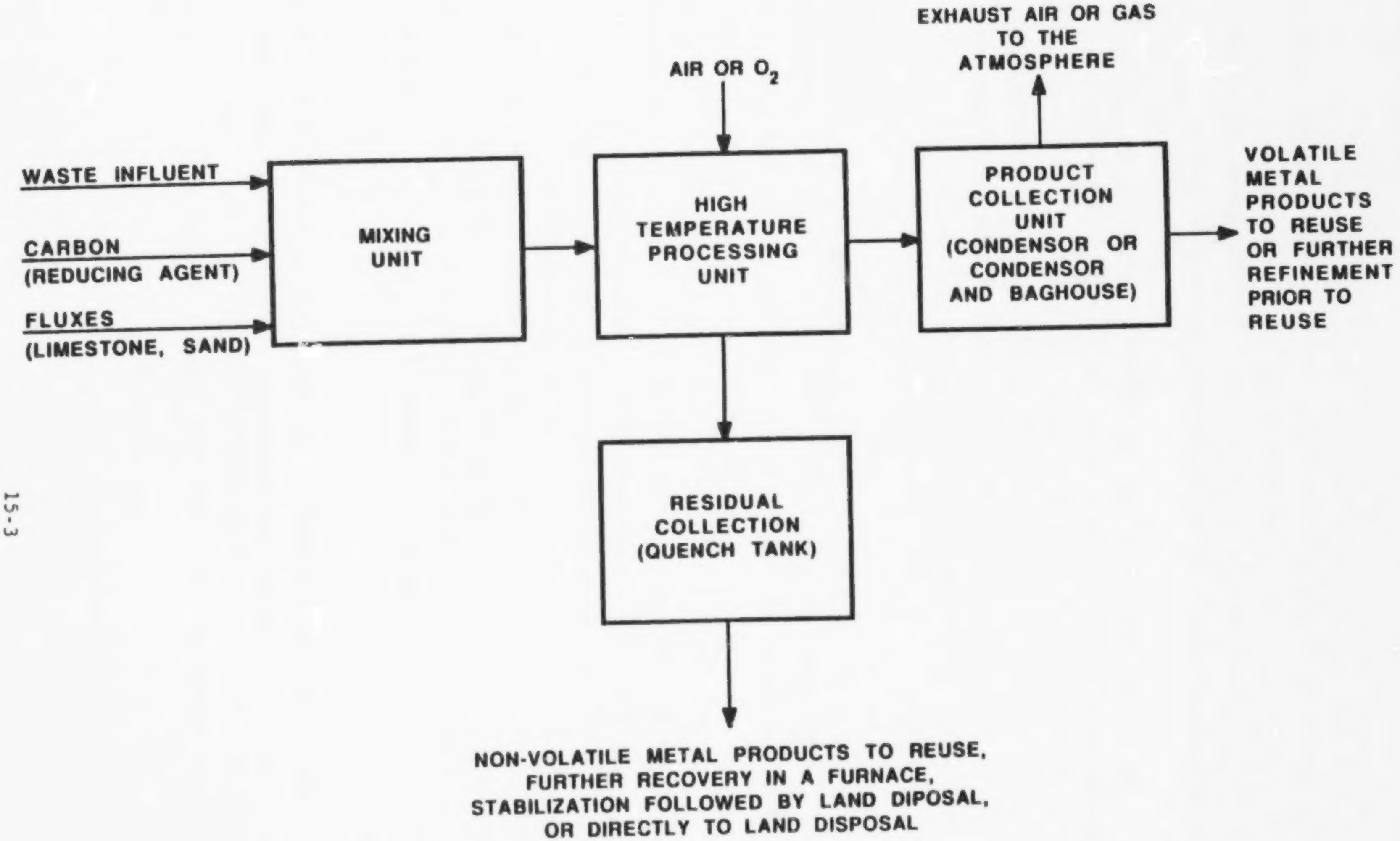
WASTE INFLUENT
CARBON (REDUCING AGENT)
FLUXES (LIMESTONE, SAND)
MIXING UNIT
AIR OR $O_2$
HIGH TEMPERATURE PROCESSING UNIT
EXHAUST AIR OR GAS TO THE ATMOSPHERE
PRODUCT COLLECTION UNIT (CONDENSOR OR CONDENSOR AND BAGHOUSE)
VOLATILE METAL PRODUCTS TO REUSE OR FURTHER REFINEMENT PRIOR TO REUSE
RESIDUAL COLLECTION (QUENCH TANK)
NON-VOLATILE METAL PRODUCTS TO REUSE, FURTHER RECOVERY IN A FURNACE, STABILIZATION FOLLOWED BY LAND DIPOSAL, OR DIRECTLY TO LAND DISPOSAL

Figure 15-1. High Temperature Metals Recovery System.

and carbon can be added to the mixing unit and mixed with the wastes. The fluxes used (sand and limestone) are often added to react with certain metal components, preventing their volatilization and resulting in an enhanced purity of the desired volatile metals removed.

The blended waste materials are fed to a furnace, where they are heated to temperatures ranging from 1100 to 1400°C (2012 to 2552°F), resulting in the reduction and volatilization of the desired metals. The combination of temperature, residence time, and turbulence provided by rotation of the unit or addition of an air or oxygen stream helps ensure the maximum reduction and volatilization of metal constituents.

The product collection system can consist of either a condenser or a combination condenser and baghouse. The choice of a particular system depends on whether the metal is to be collected in the metallic form or as an oxide. Recovery and collection are accomplished for the metallic form by condensation alone, and for the oxide by reoxidation, Figure 15-1 condensation, and subsequent collection of the metal oxide particulates in a baghouse. There is no difference in these two types of metal recovery and collection systems relative to the kinds of waste that can be treated; the use of one system or the other simply reflects the facility's preference relative to product purity. In the former case, the direct condensation of metals allows for the separation and collection of individual metals in a relatively uncontaminated form; in the latter case, the metals are collected as a combination of several metal oxides.

The treated waste residual slag, containing higher concentrations of the less-volatile metals than the untreated waste, is sometimes cooled in a quench tank and (a) reused directly as a product (e.g., a waste residual containing mostly iron can be reused in steelmaking); (b) reused after further processing (e.g., a waste residual containing oxides of iron, chromium, and nickel can be reduced to metallic form and then recovered for use in the manufacture of stainless steel); or, if the material has no recoverable value, (c) stabilized, to immobilize any remaining metal constituents, and land disposed or (d) directly land disposed as a slag.

## 15.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether high temperature metals recovery will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the concentrations of undesirable volatile metals, (b) the metal constituent boiling points, and (c) the thermal conductivity of the waste.

### 15.4.1 Concentration of Undesirable Volatile Metals

Because HTMR is a recovery process, the product must meet certain purity requirements prior to reuse. If the waste contains other volatile metals, such as arsenic or antimony, which are difficult to separate from the desired metal products and whose presence may affect the ability to reuse the product or refine it for subsequent reuse, HTMR may not be an appropriate technology. If the concentration of undesirable volatile metals in the untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 15.4.2 Metal Constituent Boiling Points

The greater the ratio of volatility of the waste constituents, the more easily the separation of these constituents can proceed. This ratio is called relative volatility. EPA recognizes, however, that the relative volatilities cannot be measured or calculated directly for the types of wastes generally treated by high temperature metals recovery. This is because the wastes usually consist of a myriad of components, all with different vapor pressure-versus-temperature relationships. However, because the volatility of components is usually inversely proportional to their boiling points (i.e., the higher the boiling point, the lower the volatility), EPA uses the boiling point of waste components as a surrogate waste characteristic for relative volatility. If the differences in boiling points between the more volatile and less volatile constituents are significantly lower in the untested waste than in the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 15.4.3 Thermal Conductivity of the Waste

The ability to heat constituents within an HTMR process feed matrix is a function of the heat transfer characteristics of the individual feed components (coke, limestone, untreated waste, etc.). The constituents being recovered from the waste must be heated to near or above their boiling points in order for them to be volatilized and recovered. The rate at which heat will be transferred to the feed mixture is dependent on the mixture's thermal conductivity, which is the ratio of the conductive heat flow to the temperature gradient across the material. Thermal conductivity measurements, as part of a treatability comparison of two different wastes to be treated by a single HTMR system, are most meaningful when applied to wastes that are homogeneous (i.e., uniform throughout). As wastes exhibit greater degrees of nonhomogeneity, thermal conductivity becomes less accurate in predicting treatability because the measurement reflects heat flow through regions having the greatest conductivity (i.e., the path of least resistance) and not heat flow through all parts of the waste. Nevertheless, EPA believes that thermal conductivity may provide the best measure of performance of heat transfer. If the thermal conductivity of the untested waste is significantly lower than that of the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 15.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of an HTMR system, EPA examines the following parameters: (a) the HTMR temperature, (b) the residence time, (c) the degree of mixing, (d) the carbon content of the feed, and (e) the calcium-to-silica ratio of the feed.

### 15.5.1 HTMR Temperature

Temperature provides an indirect measure of the energy available (i.e., Btu/hr) to volatilize the metal waste constituents. The higher the temperature in the high temperature processor, the more likely it is that the constituents will react with carbon to form free metals and volatilize. The temperature must be at least equal to or greater than the boiling point of the metals being volatilized for recovery. However, excessive temperatures could volatilize less-volatile, undesirable metals into the product, possibly inhibiting the potential for reuse of the product. EPA monitors the HTMR processor temperature continuously, if possible, to ensure that the system is operating at the appropriate design condition (at or above the boiling point(s) of the metal or metals being recovered, but not excessively high so as to volatilize other unwanted constituents) and to diagnose operational problems.

### 15.5.2 Residence Time

The residence time impacts the amount of volatile metals volatilized and recovered. It is dependent on the HTMR processor temperature and the thermal conductivity of the feed blend. EPA monitors the residence time to ensure that sufficient time is provided to effectively volatilize the volatile constituents for recovery.

### 15.5.3 Degree of Mixing

Effective mixing of the waste with coke, silica, and limestone is necessary to produce a uniform feed blend to the system. The quantifiable degree of mixing is a complex assessment that includes, among other things, the amount of energy supplied, the length of time the material is mixed, and the related turbulence effects of the specific size and shape of the tank or vessel. This is beyond the scope of simple measurement. EPA, however, evaluates the degree of mixing qualitatively by considering whether mixing is provided and whether the type of mixing device is one that could be expected to achieve uniform mixing of the waste.

### 15.5.4 Carbon Content of the Feed

The amount of carbon added to the waste must be sufficient to ensure complete reduction of the volatile metals being recovered. EPA examines the basis for calculation of the amount of carbon added to the waste to ensure that sufficient carbon is being used in the feed blend to effectively reduce metal compounds.

### 15.5.5 Calcium-to-Silica Ratio of the Feed

The calcium-to-silica ratio in the feed blend must be controlled to limit precipitation of metallic iron in the high temperature processor. The iron forms as solid calcium iron silicate, which is very difficult to subsequently process into any useful material. Aluminum oxide will also undergo reactions with lime and silica to form calcium aluminosilicates, which will lower the density and increase the volume of slag generated.

Precipitates and modified slags affect the reduction, volatilization, and recovery of volatile metals by changing heat flow characteristics in the system and by undergoing secondary, high temperature chemical reactions with metal oxides in the feed, converting them to the previously noted inert metal silicates or silicoaluminates. The ratio of calcium to silica to be used is dependent on the waste composition. Generally, a one-to-one silica-to-calcium oxide ratio is highly desired, so amounts of limestone and sand need to be adjusted based on the calcium and silica content of the waste to achieve this ratio.

Excess lime may also be added to fix sulfur in the feed as calcium sulfate. This will prevent the volatile metals from reacting with sulfur to form metal sulfides, thereby lowering the recovery of metals or oxides. EPA monitors the amounts of limestone and sand added to the waste to ensure that the calcium-to-silica ratio selected to maximize metal or oxide recovery is maintained during treatment.

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# 16. ION EXCHANGE

## 16.1 Applicability

Ion exchange is a treatment technology applicable to (1) metals in wastewaters where the metals are present as soluble ionic species (e.g., $Cr^{+3}$ and $CrO_4^{-2}$); (2) nonmetallic anions such as halides, sulfates, nitrates, and cyanides; and (3) water-soluble, ionic organic compounds including (a) acids such as carboxylics, sulfonics, and some phenols, at a pH sufficiently alkaline to yield ionic species, (b) amines, when the solution acidity is sufficiently acid to form the corresponding acid salt, and (c) quaternary amines and alkysulfates.

## 16.2 Underlying Principles of Operation

Ion exchange, when used in hazardous waste treatment, is a reversible process in which hazardous cations and/or anions are removed from an aqueous solution and are replaced by nonhazardous cations and/or anions. Ion exchange resins are cationic if they exchange positive ions (cations) and anionic if they exchange negative ions (anions). When the waste stream to be treated is brought into contact with a bed of resin beads (usually in a packed column), an exchange of hazardous ions for nonhazardous ions occurs on the surface of the resin beads. Initially, a nonhazardous ion is loosely bound to the surface of the resin. When a hazardous ion is near the resin, it is preferentially adsorbed to the surface of the resin (based on the differences in ionic potential), releasing the nonhazardous ion.

Cation exchange resins contain mobile positive ions, such as hydrogen ($H^+$) or sodium ($Na^+$), which are attached to immobile functional acid groups, such as sulfonic ($SO_3$-) and carboxylic ($COO^-$) groups. Anion exchange resins have immobile basic ions, such as amine ($NH_2^-$), to which the mobile anions, such as hydroxyl ($OH^-$) or chloride ($Cl^-$), are attached.

Ion exchange material is contacted with the solution containing the ion to be removed until the active sites in the exchange material are partially or completely used up ("exhausted") by that ion. For example, a cation exchange resin (designated $R^-$) to which a mobile positive ion ($N^+$) is attached reacts with a solution of electrolyte ($M^+X^-$) as shown below:

$$M^+X^- + R^-N^+ \rightarrow R^-M^+ + N^+ + X^-$$

After exhaustion, the resin is then contacted with a relatively low volume of a very concentrated solution of the exchange ion to convert ("regenerate") it back to its original form. The regeneration reaction may be written as follows:

$$R^-M^+ + N^+ \text{ (high concentration)} \rightarrow R^-N^+ + M^+$$

For instance, in the case of a sodium-based resin, a strong solution of sodium chloride is typically the regenerant solution. The regenerant solution forces the previously removed ions back into solution. This relatively low volume solution, now highly concentrated with the contaminant ions, must then be treated prior to disposal for recovery or removal of the hazardous cation or anion contaminants. There will continue to be a high concentration of the regenerant ion (sodium in the above example) in the used regenerant solution because excess regenerant ion is necessary to force the contaminant ions back into solution. The direction and extent of the completion of the exchange reaction depend upon the equilibrium that is established between the ions in the solution ($M^+X^-$) and those in the exchange material ($R^-N^+$).

## 16.3 Description of Ion Exchange Process

Most ion exchange operations are conducted in packed columns. The aqueous solution to be treated is continuously fed to either the top or the bottom of the column. A typical fixed-bed ion exchange column consists of a vertical cylindrical pressure vessel with corrosion-resistant linings. If appropriate, a filter is installed at the inlet of the column to remove suspended particles because they may plug the exchange resin. Spargers are provided at the top and bottom of the column to distribute waste flow. Frequently, a separate distributor is used for the regenerant solution to ensure an even flow. The resin bed, usually consisting of several feet of ion exchange resin beads, is supported by a screen near the bottom distributor or by a support bed of inert granular material. Externally, the unit has a valve manifold to permit downflow operation, upflow backwashing (to remove any suspended material), injection of the regenerant solution, and rinsing of any excess regenerant.

A typical process schematic for a basic two-step cation/anion ion exchange system is presented in Figure 16-1. The ion exchange system shown in this schematic includes a series treatment with separate cation and anion exchange systems. Some systems contain both anion and cation exchange resins in the same vessel.

The pressure vessels used for ion exchange generally range in size from 2 to 6 feet in diameter for prepackaged modular systems, which typically handle 25- to 300-gpm flow rates, to a maximum custom size of 12 feet in diameter, which can handle flow rates up to 1,150 gpm. The height of these vessels varies between 6 and 10 feet to provide adequate resin storage, distribution nozzle layout, and freeboard capacity for bed expansion during backwashing. The nominal surface loading area of the ion exchange vessels ranges from 8 to 10 gpm per square foot.

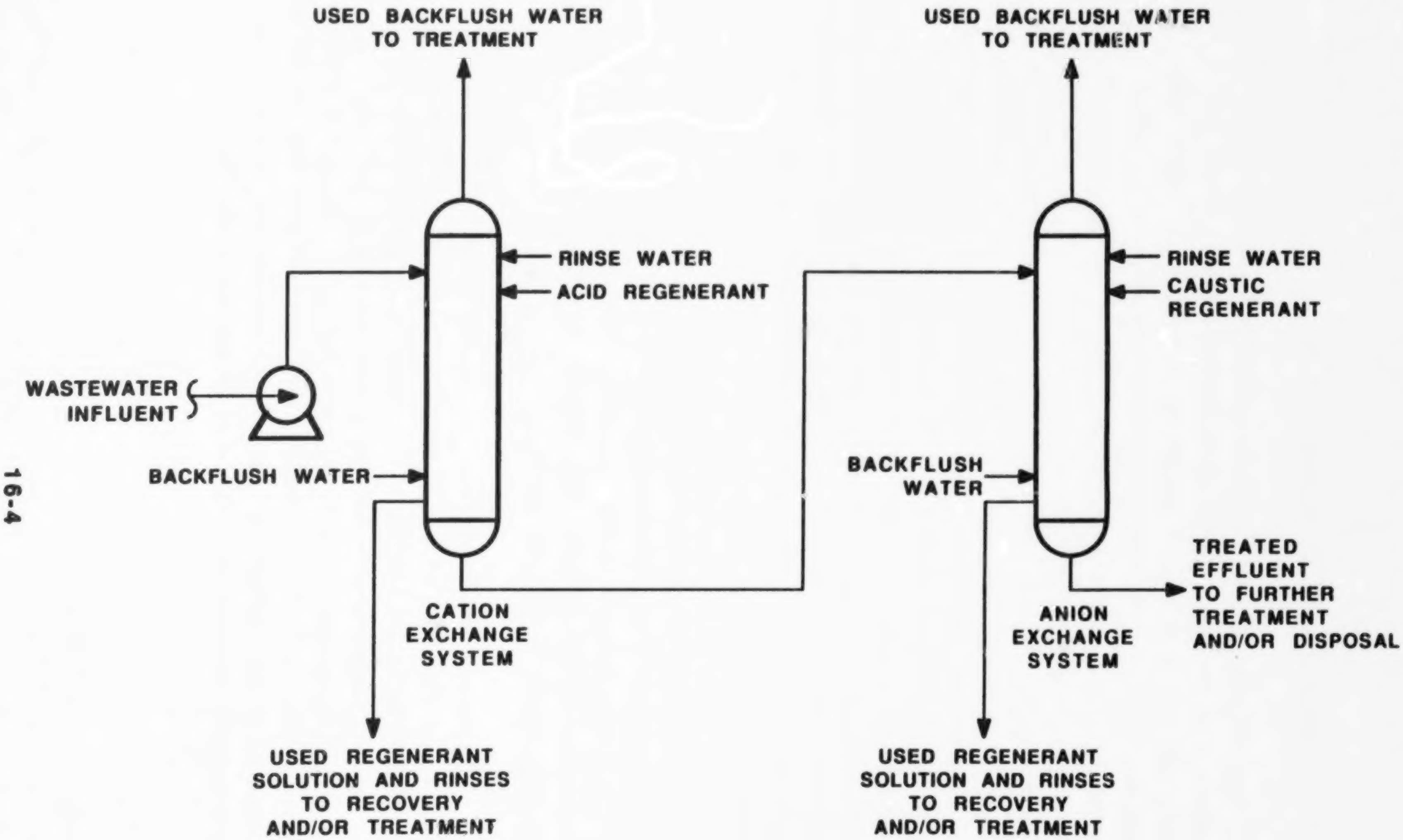
USED BACKFLUSH WATER TO TREATMENT
RINSE WATER
ACID REGENERANT
WASTEWATER INFLUENT
BACKFLUSH WATER
CATION EXCHANGE SYSTEM
USED REGENERANT SOLUTION AND RINSES TO RECOVERY AND/OR TREATMENT
USED BACKFLUSH WATER TO TREATMENT
RINSE WATER
CAUSTIC REGENERANT
BACKFLUSH WATER
ANION EXCHANGE SYSTEM
TREATED EFFLUENT TO FURTHER TREATMENT AND/OR DISPOSAL
USED REGENERANT SOLUTION AND RINSES TO RECOVERY AND/OR TREATMENT

Figure 16-1. Two Step Cation/Anion Ion Exchange System.

## 16.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether ion exchange will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the concentration and valence of the contaminant(s), (b) the concentration of competing ionic species, (c) the concentration of interfering inorganics and organics, (d) the concentrations of dissolved and suspended solids and oil and grease, and (e) the corrosiveness relative to the resin material.

### 16.4.1 Concentration and Valence of the Contaminant(s)

As the concentration and valence of adsorbable ions in the wastewater increase, the size of the resin bed required will increase as well, or, alternatively, the bed will become exhausted more rapidly. This is because a given amount of ion exchange resin has a limited number of sites to adsorb charged ions. If, for example, the valence is doubled or the concentration of the adsorbed ions is doubled, the sites will be exhausted twice as quickly. Hence, very high concentrations of the waste may be inappropriate for ion exchange because of rapid site exhaustion, which could conceivably require regenerant volumes to be essentially equal to waste flow volumes. If the concentration and/or the valence of the contaminant(s) in an untested waste is significantly higher than that of the tested waste, the system may not achieve the same performance. A larger exchange bed or more frequent regeneration may be required to exchange higher concentrations and/or higher valences of the contaminant(s) and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 16.4.2 Concentration of Competing Ionic Species

The presence of other contaminants or ions in the wastewater can affect the performance of the ion exchange unit in removing the hazardous contaminant(s) of concern. Other ions in the wastewater with the same charge as the contaminant(s) of concern will compete for exchange sites on the resin. Also, ions with a higher valence will be preferentially adsorbed. While a low concentration of the contaminant(s) of concern may be readily removed from a solution with a low concentration of other similarly charged ionic species, the contaminant(s) may not be removed as efficiently from solutions where high concentrations of similarly charged ions exist, especially if those ions have a higher valence than that of the contaminants. If the ions of concern are removed from a solution with high concentrations of other similarly charged ions, the resin will become exhausted more rapidly because most resins cannot selectively adsorb one contaminant in a solution containing other similarly charged ionic species. If the concentration of competing ionic species in an untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance. A larger exchange bed or more frequent regeneration may be required to exchange higher concentrations of competing ionic species and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 16.4.3 Concentration of Interfering Inorganics and Organics

Interfering inorganics, such as iron precipitates, can accumulate in the pores of anion exchangers; these inorganics will physically break down or block the resin particles. Some organic compounds, particularly aromatics, can be irreversibly adsorbed by the exchange resins. Also, some ions tend to oxidize after they are removed from solution. For instance, $Mn^{+2}$ (manganese) may oxidize to the insoluble $Mn^{+4}$ state, thereby permanently fouling the exchange sites and requiring the premature replacement of the resin. If the concentration of interfering inorganics and organics in an untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 16.4.4 Concentrations of Dissolved and Suspended Solids and Oil and Grease

High concentrations of dissolved and suspended solids and oil and grease can affect the performance of ion exchange sites. Conventional ion exchange systems are usually downflow, i.e., the wastewater flows down through the resin bed. Regeneration is accomplished in either the downflow or upflow mode. If excessive concentrations of dissolved and suspended solids and/or oil and grease are present in the wastewater, the bed may clog and require backwashing prior to exhausting its exchange capacity. Backwashing may prove ineffective in the removal of some solids or oils. If the concentration of dissolved and suspended solids and/or oil and grease in an untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 16.4.5 Corrosiveness

Some wastewaters are extremely corrosive to ion exchange resin materials, reducing efficiency or increasing downtime for maintenance and repair. For instance, strong solutions of chromates may oxidize many resins, requiring premature replacement. If the corrosiveness of the untested waste is significantly higher than that of the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 16.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of an ion exchange system, EPA examines the following parameters: (a) the amount and type of resin, (b) the amount and type of regenerant solution, (c) the hydraulic loading, and (d) the exchange temperature.

### 16.5.1 Amount and Type of Resin

The main design parameter that affects the performance of ion exchange systems is the amount and type of resin used. Numerous cationic and anionic resins are commercially available. The selection of a resin is based on a variety of factors. Different resins have different exchange capacities, and some have greater affinity than others for specific ions. Certain resins are designed to tolerate corrosive, oxidizing, or high temperature solutions, so their exchange capacity does not degrade as rapidly with use. Most resins will effectively remove contaminant ions from solution until they become exhausted. However, if resin bed exhaustion occurs too frequently, or if regeneration requires excessive volumes of the regenerant, the type and/or amount of resin might need to be changed. In some instances, pretreatment technologies may be required prior to ion exchange. For most metals removal, cation resins are usually required. However, some metal complexes, such as copper cyanide ($Cu(CN)_4^{-2}$), chromates ($CrO_4^{-2}$), and arsenates ($AsO_4^{-3}$), are anionic and require the use of anion exchange resins. EPA examines the amount and type of ion exchange resin in the treatment system to ensure that a sufficient amount of ion exchange resin is provided to effectively exchange the metal ions of concern.

### 16.5.2 Amount and Type of Regenerant Solution

For hydrogen-based cation exchangers, acid regenerant solutions are used (e.g., sulfuric, nitric, or hydrochloric acids). For sodium-based cation resins, sodium chloride is generally used. For anion exchange resins, alkali (commonly sodium hydroxide) is used to regenerate hydroxide-based resins. Sodium chloride is used for chloride-based anion resins. EPA examines the amount and type of regenerant solution used to ensure that it is compatible with the resin and waste treated and that effective removal of the contaminant ions from the exchange resin is achieved.

### 16.5.3 Hydraulic Loading Rate

The amount of time that the wastewater contaminants are in contact in the ion exchange resin (i.e., residence time) impacts the extent to which ion exchange occurs. Higher residence times generally improve exchange performance, but require larger ion exchange beds to maintain the same overall throughput. For a given size ion exchange bed, the residence time can be determined by the hydraulic loading rate. Typical hydraulic loading rates for ion exchange systems range from 600 to 15,000 gal/day-ft$^2$. EPA monitors the hydraulic loading rate to ensure that sufficient time is provided to effectively exchange contaminants.

### 16.5.4 Exchange Temperature

High temperatures reduce resin life, requiring premature replacement. EPA monitors the temperature in an ion exchange column continuously, if possible, to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

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# 17. RETORTING

## 17.1 Applicability

Retorting is a treatment technology applicable to wastes containing elemental mercury, as well as mercury present in the oxide, hydroxide, and sulfide forms, at levels above 100 parts per million, provided that the waste has a low total organic content (i.e., below 1 percent). For metals other than mercury, the typical retort operating temperatures (700 to 1000°F) are not high enough to decompose the metal compounds. High temperature metals recovery (HTMR) processes must be used to recover most other metals when they are not present in the pure metal form.

For most retorting processes, there is an additional requirement that the waste have a low water content, preferably below 20 percent. Dewatering reduces energy consumption by minimizing the amount of water evaporated and precludes problems involving the separation of recovered metals from large quantities of water.

## 17.2 Underlying Principles of Operation

The basic principle of operation for retorting is a process similar to that for high temperature metals recovery in that it provides for recovery of metals from wastes primarily by volatilization and subsequent collection and condensation of the volatilized components. Retorting yields a metal product for reuse and significantly reduces the concentration of metals in the waste residual, and, hence, the amount of treated waste that needs to be land disposed. This technology is different from HTMR in that HTMR includes a reduction reaction involving the use of carbon, while retorting does not use a reducing agent. Additionally, this process differs with regard to the form and, possibly, the leachability of the residue generated; HTMR generates a slag, while retorting generates a granular solid residue that may have lower leachability than a slag if mercury is the only constituent of concern present in the untreated waste.

The basic principle of operation of retorting is that sufficient heat must be transferred to the waste to cause elemental metals to vaporize. In the case of mercury present as an oxide, hydroxide, or sulfide compound, sufficient heat must be transferred to the waste to first decompose the compounds to the elemental form and then volatilize the mercury. In mercury wastes that are wastewater treatment sludges, mercury is most often present in the form of the sulfide (HgS) as a result of the use of sodium hydrosulfide treatment of mercury-bearing wastewaters. In a few instances, hydrazine is used to treat these same wastewaters; in such instances, a mercurous hydroxide sludge is generated. This latter compound can be more easily treated to yield elemental mercury because this reaction occurs more readily than the sulfide decomposition at the temperatures at which the process is normally operated. Preheated air is provided to the retort to supply the oxygen necessary for the sulfide decomposition and to enhance the heat transfer to the waste.

The equations for decomposition of both forms of mercury are presented below:

(a) $HgS + O_2 \rightarrow Hg + SO_2$

(b) $2Hg_2(OH)_2 \rightarrow 4Hg + 2H_2O + O_2$.

## 17.3 Description of Retorting Process

The retorting process generally consists of a retort (typically an oven) in which the waste is heated to volatilize the metal constituents, a condenser, a metals collection system, and an air pollution control system. Figures 17-1 and 17-2 show a retort system without and with a scrubber-type air pollution control system.

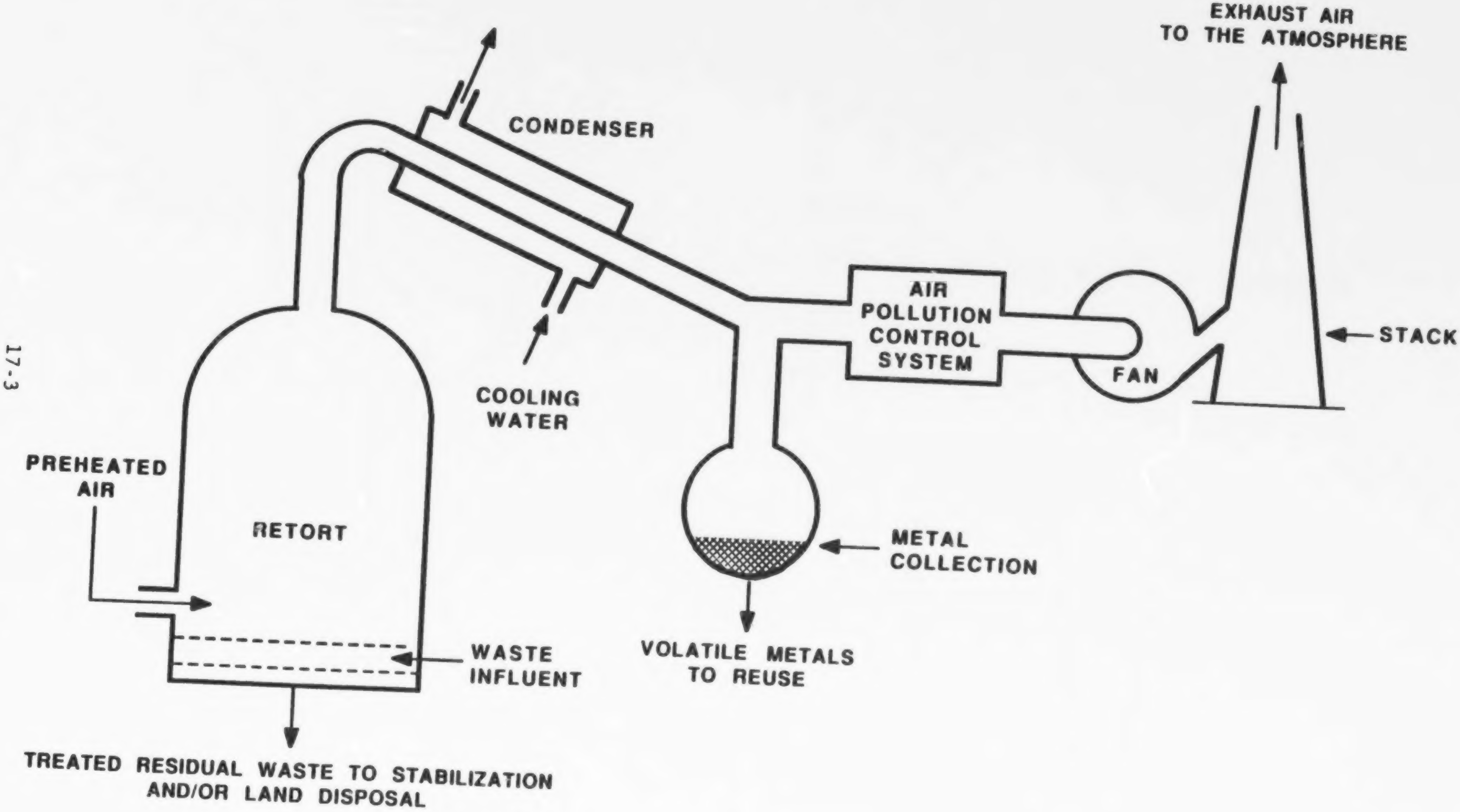
EXHAUST AIR
TO THE ATMOSPHERE
CONDENSER
AIR
POLLUTION
CONTROL
SYSTEM
STACK
FAN
COOLING
WATER
PREHEATED
AIR
RETORT
METAL
COLLECTION
WASTE
INFLUENT
VOLATILE METALS
TO REUSE
TREATED RESIDUAL WASTE TO STABILIZATION
AND/OR LAND DISPOSAL

Figure 17-1. Retorting Process (Without a Scrubber and Subsequent Wastewater Discharge).

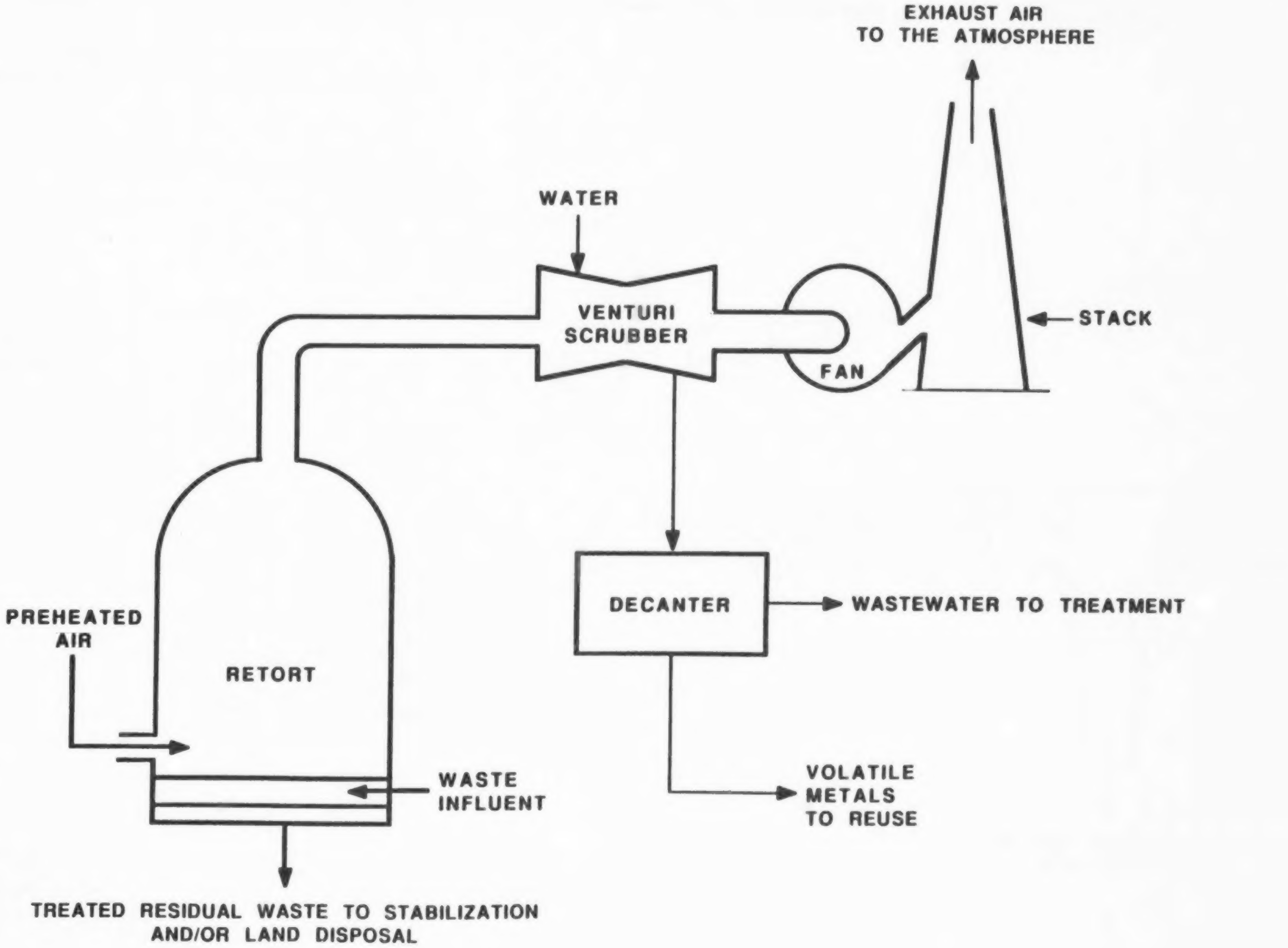
EXHAUST AIR
TO THE ATMOSPHERE
WATER
VENTURI
SCRUBBER
FAN
STACK
PREHEATED
AIR
RETORT
DECANTER
WASTEWATER TO TREATMENT
WASTE
INFLUENT
VOLATILE
METALS
TO REUSE
TREATED RESIDUAL WASTE TO STABILIZATION
AND/OR LAND DISPOSAL

Figure 17-2. Retorting Process (With a Scrubber and Subsequent Wastewater Discharge).

Trays of wastes are placed in the retort, where they are heated, and decomposition of mercury compounds and volatilization of the metallic mercury and other volatile elemental metals occur. Although most commonly carried out in an oven, retorting can also be performed in a multiple hearth furnace.

The vapor stream from the retort is either cooled in a condenser. If a scrubber is not used as an air pollution control device, an electrostatic precipitator is provided after the condenser to remove any residual metal in the exhaust vapor stream, as well as to control other potential emissions such as sulfur dioxide ($SO_2$), fly ash, and hydrogen chloride (HCl) vapors. Condensed metal is collected for reuse before the electrostatic precipitator.

Residual solids remaining in the retort, stripped of volatile metal contaminants, are collected and may be either directly land disposed or stabilized, to immobilize any remaining metal constituents, and then land disposed.

## 17.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether retorting will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the concentration of undesirable volatile constituents in the waste and (b) the thermal conductivity of the waste.

### 17.4.1 Concentration of Undesirable Volatile Constituents

Because retorting is a recovery process, its product must meet certain purity requirements prior to reuse. If the waste contains other volatile constituents with boiling points equal to or below that of the metal(s) to be recovered, they will be volatilized and condensed along with the desired metal(s) present in the waste. These constituents may be difficult to separate from the recovered product and may affect the ability to reuse the product metal or refine it for subsequent reuse. Undesirable volatile constituents sometimes present in mercury-bearing wastes include (a) mercury chlorides, which distill unchanged in the retorting process, and other volatile metal halides; (b) arsenic oxide and arsenic trichloride; and (c) organomercury compounds, such as phenylmercuric acetate, which are not decomposed to elemental mercury by the retorting process.

For wastes containing significant levels (i.e., above 1 percent) of these contaminants, retorting may not be an appropriate technology. If the concentration of undesirable volatile constituents in the untested waste is significantly higher than that in the tested waste, the system may not achieve the same performance. Chemical pretreatment may be required to convert mercury chlorides and organomercury compounds to mercuric sulfide and/or elemental mercury and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 17.4.2 Thermal Conductivity of the Waste

The ability to heat constituents within a waste matrix is a function of the heat transfer characteristics of the waste material. Mercury and other recoverable metals in the waste must be heated to near or above their boiling points in order to be volatilized and recovered. The rate at which heat will be transferred to the waste material is dependent on the material's thermal conductivity, which is the ratio of the conductive heat flow to the temperature gradient across the material. Thermal conductivity measurements, as part of a treatability comparison of two different wastes to be treated by a single retort system, are most meaningful when applied to wastes that are homogeneous (i.e., uniform throughout). As wastes exhibit greater degrees of nonhomogeneity, thermal conductivity becomes less accurate in predicting treatability because the measurement reflects heat flow through regions having the greatest conductivity (i.e., the path of least resistance) and not heat flow through all parts of the waste. Nevertheless, EPA believes that thermal conductivity may provide the best measure of performance of heat transfer. If the thermal conductivity of the untested waste is significantly lower than that of the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 17.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a retort system, EPA examines the following parameters: (a) the retorting temperature and (b) the residence time.

### 17.5.1 Retorting Temperature

Temperature provides an indirect measure of the energy available (i.e., Btu/hr) to vaporize the metal of concern. The higher the temperature in the retort, the more likely it is that the metal will volatilize. The temperature must be at least equal to or greater than the boiling point of the metal. However, excessive temperatures could volatilize undesirable constituents into the product, possibly inhibiting its potential reuse. For mercury retorting, EPA monitors the retort temperature to ensure that the system is operating at the appropriate design condition (a temperature at least equal to the boiling point of mercury (674°F) but below 1000°F) and to diagnose operational problems.

### 17.5.2 Residence Time

The residence time impacts the amount of volatile metal(s) volatilized and recovered. It is dependent on the retort temperature and the thermal conductivity of the waste. Typical residence times in retort systems for mercury range from 4 hours to 20 hours. EPA monitors the residence time to ensure that sufficient time is provided to effectively volatilize all of the mercury and/or other metal(s) to be removed from the waste.

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# 18. STABILIZATION OF METALS

## 18.1 Applicability

Stabilization is a treatment technology applicable to wastes containing leachable metals and having a high filterable solids content, low total organic carbon (TOC) content, and low oil and grease content. This technology is commonly used to treat residuals generated from treatment of electroplating wastewaters and incineration ash residues. For wastes with recoverable levels of metals, high temperature metals recovery and retorting technologies may be applicable.

Stabilization refers to a broad class of treatment processes that immobilize hazardous constituents in a waste. Solidification and fixation are other terms that are sometimes used synonymously for stabilization or to describe specific variations within the broader class of stabilization. Related technologies are encapsulation and thermoplastic binding. However, EPA considers these technologies to be distinct from stabilization in that their operational principles are significantly different.

## 18.2 Underlying Principles of Operation

The basic principle of operation for stabilization is that leachable metals in a waste are immobilized following the addition of stabilizing agents and other chemicals. The reduced leachability is accomplished by the formation of a lattice structure and/or chemical bonds that bind the metals to the solid matrix and thereby limit the amount of metal constituents that can be leached when water or a mild acid solution comes into contact with the waste material.

The two principal stabilization processes used are cement-based and lime/pozzolan-based processes. A brief discussion of each is provided below. In both cement-based or lime/pozzolan-based techniques, the stabilizing process can be modified through the use of additives, such as silicates, that control curing rates, reduce permeability, and enhance the properties of the solid material.

### 18.2.1 Portland Cement-Based Process

Portland cement is a mixture of powdered oxides of calcium, silica, aluminum, and iron, produced by kiln burning of materials rich in calcium and silica at high temperatures (i.e., 1,400 to 1,500°C (2,552 to 2,732°F)). When the anhydrous cement powder is mixed with water, hydration occurs and the cement begins to set. The chemistry involved is complex because many different reactions occur depending on the composition of the cement mixture.

As the cement begins to set, a colloidal gel of indefinite composition and structure is formed. Over time, the gel swells and forms a matrix composed of interlacing, thin, densely packed silicate fibrils. Constituents present in the waste slurry (e.g., hydroxides and carbonates of various metals) are incorporated into the interstices of the cement matrix. The high pH of the cement mixture tends to keep metals in the form of insoluble hydroxide and carbonate salts. It has been hypothesized that metal ions may also be incorporated into the crystal structure of the cement matrix, but this hypothesis has not been verified.

### 18.2.2 Lime/Pozzolan-Based Process

Pozzolan, which contains finely divided, noncrystalline silica (e.g., fly ash or components of cement kiln dust), is a material that is not cementitious in itself, but becomes so upon the addition of lime. Metals in the waste are converted to insoluble silicates or hydroxides and are incorporated into the interstices of the binder matrix, thereby inhibiting leaching.

## 18.3 Description of Stabilization Process

The stabilization process consists of a weighing device, a mixing unit, and a curing vessel or pad. Commercial concrete mixing and handling equipment is typically used in stabilization processes. Weighing conveyors, metering cement hoppers, and mixers similar to concrete batching plants have been adapted in some operations. When extremely dangerous materials are treated, remote-control and in-drum mixing equipment, such as is used with nuclear waste, is employed.

In most stabilization processes, the waste, stabilizing agent, and other additives, if used, are mixed in a mixing vessel and then transferred to a curing vessel or pad and allowed to cure. The actual operation (equipment requirements and process sequencing) depends on several factors including the nature of the waste, the quantity of the waste, the location of the waste in relation to the disposal site, the particular stabilization formulation used, and the curing rate. Following curing, the stabilized solid formed is recovered from the processing equipment and disposed of.

## 18.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether stabilization will achieve the same level of performance on an untested waste as on a previously tested waste, and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the concentration of fine particulates, (b) the concentration of oil and grease, (c) the concentration of organic compounds, and (d) the concentration of sulfate and chloride compounds.

### 18.4.1 Concentration of Fine Particulates

For both cement-based and lime/pozzolan-based processes, very fine solid materials (i.e., those that pass through a No. 200 mesh sieve (less than 74 um particle size)) weaken the bonding between waste particles and the cement or lime/pozzolan binder by coating the particles. This coating inhibits chemical bond formation, thereby decreasing the resistance of the material to leaching. If the concentration of fine particulates in an untested waste is significantly higher than in the tested waste, the system may not achieve the same performance. Pretreatment of the waste may be required to reduce the fine particulate concentration and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 18.4.2 Concentration of Oil and Grease

Oil and grease in both cement-based and lime/pozzolan-based systems results in the coating of waste particles and the weakening of the bonding between the particle and the stabilizing agent, thereby decreasing the resistance of the material to leaching. If the concentration of oil and grease in the untested waste is significantly higher than in the tested waste, the system may not achieve the same performance. Pretreatment may be required to reduce the oil and grease concentration and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 18.4.3 Concentration of Organic Compounds

Organic compounds in the waste interfere with the stabilization chemical reactions and bond formation, thus inhibiting curing of the stabilized material. This results in a stabilized waste having decreased resistance to leaching. If the total organic carbon (TOC) content of the untested waste is significantly higher than that of the tested waste, the system may not achieve the same performance. Pretreatment may be required to reduce the TOC and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 18.4.4 Concentration of Sulfate and Chloride Compounds

Sulfate and chloride compounds interfere with the stabilization chemical reactions, weakening bond strength and prolonging setting and curing time. Sulfate and chloride compounds may reduce the dimensional stability of the cured matrix, thereby increasing leachability potential. If the concentration of sulfate and chloride compounds in the untested waste is significantly higher than in the tested waste, the system may not achieve the same performance. Pretreatment may be required to reduce the sulfate and chloride concentrations and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 18.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a stabilization system, EPA examines the following parameters: (a) the amount and type of stabilizing agent and additives, (b) the degree of mixing, (c) the residence time, and (d) the stabilization temperature and humidity.

### 18.5.1 Amount and Type of Stabilizing Agent and Additives

The stabilizing agent and additives used will determine the chemistry and structure of the stabilized material and therefore its leachability. Stabilizing agents and additives must be carefully selected based on the chemical and physical characteristics of the waste to be stabilized. To select the most effective type of stabilizing agent and additives, the waste should be tested in the laboratory with a variety of these materials to determine the best combination.

The amount of stabilizing agent and additives is a critical parameter in that sufficient stabilizing materials are necessary to properly bind the waste constituents of concern, making them less susceptible to leaching. The appropriate weight ratios of stabilizing agent and additives to waste are established empirically by setting up a series of laboratory tests that allow separate leachate testing of different mix ratios. The ratio of water to stabilizing agent (including water in waste) will also impact the strength and leaching characteristics of the stabilized material. Too much water will cause low strength; too little will make mixing difficult and, more important, may not allow the chemical reactions that bind the hazardous constituents to be fully completed. EPA evaluates the amount of stabilizing agent, water, and other additives used in the stabilization process to ensure that sufficient stabilizing materials are added to the waste to effectively immobilize the waste constituents of concern.

### 18.5.2 Degree of Mixing

Mixing is necessary to ensure homogeneous distribution of the waste, stabilizing agent, and additives. Both undermixing and overmixing are undesirable. The first condition results in a nonhomogeneous mixture;

therefore, areas will exist within the waste where waste particles are neither chemically bonded to the stabilizing agent nor physically held within the lattice structure. Overmixing, on the other hand, may inhibit gel formation and ion adsorption in some stabilization systems. Optimal mixing conditions generally are determined through laboratory tests. The quantifiable degree of mixing is a complex assessment that includes, among other things, the amount of energy supplied, the length of time the material is mixed, and the related turbulence effects of the specific size and shape of the mix tank or vessel. This is beyond the scope of simple measurement. EPA, however, evaluates the degree of mixing qualitatively by considering whether mixing is provided and whether the type of mixing deice is one that could be expected to achieve homogeneous distribution of the waste, stabilizing agent, and additives.

### 18.5.3 Residence Time

The residence time or duration of curing ensures that the waste particles have had sufficient time in which to incorporate into lattice structures and/or form stable chemical bonds. The time necessary for complete stabilization depends upon the waste and the stabilization process used. The performance of the stabilized waste (i.e., the levels of waste constituents in the leachate) will be highly dependent upon whether complete stabilization has occurred. Typical residence times range from 7 to 28 days. EPA monitors the residence time to ensure that sufficient time is provided to effectively stabilize the waste.

### 18.5.4 Stabilization Temperature and Humidity

Higher temperatures and lower humidity increase the rate of curing by increasing the rate of evaporation of water from the stabilization mixtures. If temperatures are too high, however, the evaporation rate can be excessive and result in too little water being available for completion of the stabilization reaction. EPA monitors the stabilization temperature and humidity continuously, if possible, to ensure that the system is operating at the appropriate design conditions and to diagnose operational problems.

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# 19. CHEMICAL OXIDATION

## 19.1 Applicability

Chemical oxidation is a treatment technology used to treat wastes containing organics. In addition, it is used to treat sulfide wastes by converting the sulfide to sulfate. Also, the destruction of cyanides in wastes can be accomplished by chemical oxidation.

Chemical oxidation of cyanide is applicable for dissolved cyanides in aqueous solutions, such as wastewaters from metal plating and finishing operations, or for inorganic sludges from these operations that contain soluble cyanide compounds. Chemical oxidation is most applicable to cyanides that are in a form that can be easily disassociated in water to yield free cyanide ions. If the cyanide is present in water as a tightly bound complex ion (e.g., ferrocyanide), only limited treatment may occur.

Chemical oxidation may also be used in treatment of complexed metal wastes. Organic compounds such as EDTA, NTA, citric acid, glutaric acid, lactic acid, and tartrates are often used as chelating agents to prevent metal ions from precipitating out in electroless plating solutions. When these spent plating solutions require treatment for metals removal by chemical precipitation, the organic chelating agents must first be destroyed. Chemical oxidants, potassium permanganate in particular, are effective in releasing metals from complexes with these organic compounds.

## 19.2 Underlying Principles of Operation

The basic principle of operation for chemical oxidation is that inorganic cyanides, some dissolved organic compounds, and sulfides can be chemically oxidized to yield carbon dioxide, water, salts, simple organic acids, and, in the case of sulfides, sulfates. The principal chemical oxidants used are hypochlorite, chlorine gas, chlorine dioxide, hydrogen peroxide, ozone, and potassium permanganate. The reaction chemistry for each is discussed below.

### 19.2.1 Oxidation with Hypochlorite or Chlorine (Alkaline Chlorination)

This type of oxidation is carried out using sodium hypochlorite (NaOCl), calcium hypochlorite ($Ca(OCl)_2$), chlorine gas ($Cl_2$), or sometimes chlorine dioxide gas ($ClO_2$). The reactions are normally conducted under slightly or moderately alkaline conditions. Alkaline chlorination of cyanide is a two-step process usually operated at a pH of 10 to 11.5 for the first step and 8.5 for the second step. The toxic gas cyanogen chloride (CNCl) is formed as a reaction intermediate in the first step of this process and may be liberated if the pH is less than 10 and incomplete reaction occurs. Example reactions for the oxidation of cyanide, phenol, and sulfide using sodium hypochlorite are shown below:

Cyanide: $CN^- + NaOCl \rightarrow OCN^- + NaCl$ (Step 1)

$2OCN^- + 3NaOCl \rightarrow CO_3^{2-} + CO_2 + N_2 + 3NaCl$ (Step 2)

Phenol: $C_6H_5OH + 14NaOCl \rightarrow 6CO_2 + 3H_2O + 14NaCl$

Sulfide: $S^= + 4NaOCl \rightarrow SO_4^= + 4NaCl$

Chlorine dioxide also oxidizes the same pollutants under identical conditions. Chlorine dioxide first hydrolyzes to form a mixture of chlorous ($HClO_2$) and chloric ($HClO_3$) acids. These acids act as the oxidants, as shown in the equations below, for phenol:

$$2ClO_2 + H_2O \rightarrow HClO_2 + HClO_3$$

$$C_6H_5OH + 7HClO_2 \rightarrow 6CO_2 + 3H_2O + 7HCl$$

$$3C_6H_5OH + 14HClO_3 \rightarrow 8CO_2 + 9H_2O + 14HCl$$

### 19.2.2 Peroxide Oxidation

Peroxide oxidizes the same constituents that alkaline chlorination oxidizes under similar conditions. The relevant reactions are:

Cyanide: $2CN^- + 5H_2O_2 \rightarrow 2CO_2 + N_2 + 4H_2O + 2OH^-$

Phenol: $C_6H_5OH + 14H_2O_2 \rightarrow 6CO_2 + 17H_2O$

Sulfide: $S^= + 4H_2O_2 \rightarrow SO_4^= + 4H_2O$

### 19.2.3 Oxidation with Ozone (Ozonation)

Ozone is an effective oxidizing agent for treatment of organic compounds and for the oxidation of cyanide to cyanate. Cyanogen gas ($C_2N_2$) is a reaction intermediate in this reaction. Further oxidation of cyanate to carbon dioxide and nitrogen compounds ($N_2$ or $NH_3$) occurs slowly with ozone. The oxidation of cyanide to cyanate proceeds by the following reaction:

$$CN^- + O_3 \rightarrow CNO^- + O_2$$

The rates of ozonation reactions can be accelerated by supplying ultraviolet (UV) radiation during treatment. Some literature sources indicate that even the most difficult cyanide complexes to treat, the iron-cyanide complexes, can be oxidized completely.

### 19.2.4 Oxidation with Potassium Permanganate

Potassium permanganate can also be used to oxidize the same constituents as the other chemical oxidants. The reactions of potassium permanganate with phenol and sulfide at acidic pHs and with cyanide at pH 12 to 14 are as follows:

Phenol: $3C_6H_5OH + 28KMnO_4 + 28H^+ \rightarrow 18CO_2 + 28MnO_2 + 23H_2O + 28K^+$

Sulfide: $5S^= + 8KMnO_4 + 24H^+ \rightarrow 5SO_4^= + 8Mn^{+2} + 12H_2O + 8K^+$

Cyanide: $CN^- + 2KMnO_4 + Ca(OH)_2 \rightarrow CNO^- + K_2MnO_4 + CaMnO_4 + H_2O$

In cyanide oxidation using potassium permanganate, cyanide is oxidized only to cyanate. Further oxidation of cyanate can be accomplished by acid hydrolysis or by the use of another oxidizing agent.

### 19.2.5 $SO_2$/Air Oxidation

Cyanide can be oxidized to cyanate in an aqueous solution by bubbling air containing from 1 to 10 percent $SO_2$ through the waste. The $SO_2$ is also oxidized to sulfate in this reaction. This treatment process occurs by the following reaction:

$$CN^- + SO_2 + O_2 + H_2O \rightarrow CNO^- + H_2SO_4$$

This oxidation reaction requires the use of a soluble copper salt catalyst. Copper sulfate ($CuSO_4$) is most often used. $SO_2$/air oxidation is used frequently in the treatment of wastewaters from gold production, which contain both cyanide and thiocyanate, because $SO_2$/air oxidizes cyanide more strongly than thiocyanate while alkaline chlorination and other common oxidizing agents oxidize thiocyanate more strongly than cyanide. As with potassium permanganate, further oxidation of cyanate can be accomplished by acid hydrolysis or by the use of another oxidizing agent.

## 19.3 Description of Chemical Oxidation Processes

### 19.3.1 Alkaline Chlorination

Alkaline chlorination can be accomplished by either batch or continuous processes. For batch treatment, the wastewater is transferred to a reaction tank, where the pH is adjusted and the oxidizing agent is added. In some cases, the tank may be heated to increase the reaction rate. For oxidation of most compounds, a slightly to moderately alkaline pH is used. It is important that the tank be well mixed for effective treatment to occur. After treatment, the wastewater is either directly discharged or transferred to another process for further treatment.

In the continuous process, automatic instrumentation is used to control pH, reagent addition, and temperature. An oxidation-reduction potential (ORP) sensor is usually used to measure the extent of reaction.

In both types of processes, agitation is typically provided to maintain thorough mixing. Typical residence times for these and other oxidation processes range from 1 to 2 hours.

### 19.3.2 Peroxide Oxidation

The peroxide oxidation process is run under similar conditions, and with similar equipment, to those used in the alkaline chlorination process. Hydrogen peroxide is added as a liquid solution.

### 19.3.3 Ozonation

Ozonation can be conducted in a batch or continuous process. The ozone for treatment is produced onsite because of the hazards of transporting and storing ozone as well as its short shelf life. The ozone gas is supplied to the reaction vessels by injection into the wastewater. The batch process uses a single reaction tank. As with alkaline chlorination, the amount of ozone added and the reaction time used are determined by the type and concentration of the oxidizable contaminants, and vigorous mixing should be provided for complete oxidation.

In continuous operation, two separate tanks may be used for reaction. The first tank receives an excess dosage of ozone. Any excess ozone remaining at the outlet of the second tank is recycled to the first tank, thus ensuring that an excess of ozone is maintained and also that no ozone is released to the atmosphere. As with alkaline chlorination, an ORP control system is usually necessary to ensure that sufficient ozone is being added.

### 19.3.4 Permanganate Oxidation

Permanganate oxidation is conducted in tanks in a manner similar to that used for alkaline chlorination, as discussed previously. Potassium permanganate is normally dissolved in an auxiliary tank and added as a solution. As with the other oxidizing agents, ORP (for continuous processes) and excess oxidizing agent (for batch processes) are monitored to measure the extent of reaction.

### 19.3.5 $SO_2$/Air Oxidation

$SO_2$/air oxidation of cyanide depends on efficient mixing of air with the waste to ensure an adequate supply of oxygen. Because of this factor, the equipment requirements for this process are similar to those of ozonation. $SO_2$ is sometimes supplied with the air by using flue gas containing $SO_2$ as the air source. Otherwise, sulfur in the +4 oxidation state can be fed as gaseous sulfur dioxide ($SO_2$), liquid sulfurous acid ($H_2SO_3$), sodium sulfite ($Na_2SO_3$) solution, or sodium bisulfite ($NaHSO_3$) solution. Sodium bisulfite solution, made by dissolving sodium metabisulfite ($Na_2S_2O_5$) in water, is the most frequently used source of $SO_2$. This process is usually run continuously, with the addition of oxidizing agent and acid/alkali being controlled through continuous monitoring of ORP and pH, respectively.

## 19.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether chemical oxidation will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the concentration of other oxidizable contaminants and (b) the concentration of metal salts.

### 19.4.1 Concentration of Other Oxidizable Compounds

The presence of other oxidizable compounds in addition to the constituents of concern will increase the demand for oxidizing agents and, hence, potentially reduce the effectiveness of the treatment process. As a surrogate for the amount of oxidizable organics present, EPA analyzes for total organic carbon (TOC) in the waste. Inorganic reducing compounds such as sulfide may also create a demand for additional oxidizing agent;

EPA also attempts to identify and analyze for these constituents. If TOC and/or inorganic reducing compound concentrations in the untested waste are significantly higher than those in the tested waste, the system may not achieve the same performance. Additional oxidizing agent may be required to effectively oxidize the waste and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 19.4.2 Concentration of Metal Salts

Metal salts, especially lead and silver salts, will react with the oxidizing agent(s) to form metal peroxides, chlorides, hypochlorites, and/or chlorates. These reactions can cause an excessive consumption of oxidizing agents and potentially interfere with the effectiveness of treatment.

An additional problem with metals in cyanide solutions is that metal-cyanide complexes are sometimes formed. These complexes are negatively charged metal-cyanide ions that are extremely soluble. Cyanide in the complexed form may not be oxidizable, depending on the strength of the metal-cyanide bond in the complex and the type of oxidizing agent used. Iron complexes (for example, the ferrocyanide ion, $Fe(CN)_6^{-4}$) are the most stable of the complexed cyanides.

If the concentrations of metal salts and/or metal-cyanide complexes in the untested waste are significantly higher than those in the tested waste, the system may not achieve the same performance. Additional oxidizing agent and/or a different oxidizing agent may be required to effectively oxidize the waste and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 19.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a chemical oxidation system, EPA examines the following parameters: (a) the residence time, (b) the amount and type of oxidizing agent, (c) the degree of mixing, (d) the pH, (e) the oxidation temperature, and (f) the amount and type of catalyst.

### 19.5.1 Residence Time

The residence time impacts the extent of volatilization of waste contaminants. For a batch system, the residence time is controlled by adjusting the treatment time in the reaction tank. For a continuous system, the waste feed rate is controlled to make sure that the system is operated at the appropriate design residence time. EPA monitors the residence time to ensure that sufficient time is provided to effectively oxidize the waste.

### 19.5.2 Amount and Type of Oxidizing Agent

Several factors influence the choice of oxidizing agents and the amount to be added. The amount of oxidizing agent required to treat a given amount of oxidizable constituent(s) will vary with the agent chosen. Enough oxidant must be added to ensure complete oxidation; the specific amount will depend on the type of oxidizable compounds in the waste and the chemistry of the oxidation reactions. Theoretically, the amount of oxidizing agent to be added can be computed from oxidation reaction stoichiometry; in practice, an excess of oxidant should be used. Testing for excess oxidizing agent will determine whether the reaction has reached completion. In continuous processes, the addition of oxidizing agent is accomplished by automated feed methods. The amount of oxidizing agent needed is usually measured and controlled automatically by an oxidation-reduction potential (ORP) sensor. EPA examines the amount of oxidant added to the chemical oxidation system to ensure that it is sufficient to effectively oxidize the waste and, for continuous processes, examines how the facility ensures that the particular addition rate is maintained. EPA also tests for excess oxidizing agent for batch processes and continuously monitors the ORP for continuous processes to ensure that excess oxidizing agent, if possible, is supplied.

### 19.5.3 Degree of Mixing

Process tanks must be equipped with mixers to ensure maximum contact between the oxidizing agent and the waste solution. Proper mixing also limits the production of any solid precipitates from side reactions that may resist oxidation. Mixing also provides an even distribution of tank contents and a homogeneous pH throughout the waste, improving oxidation of wastewater constituents. The quantifiable degree of mixing is a complex assessment that includes, among other things, the amount of energy supplied, the length of time the material is mixed, and the related turbulence effects of the specific size and shape of the tank. This is beyond the scope of simple measurement. EPA, however, evaluates the degree of mixing qualitatively by considering whether mixing is provided and whether the type of mixing device is one that could be expected to achieve uniform mixing of the waste solution.

### 19.5.4 pH

Operation at the optimal pH maximizes the chemical oxidation reactions and may, depending on the oxidizing agent being used, limit the formation of undesirable reaction byproducts or the escape of cyanide from solution as HCN, CNCl, or $C_2N_2$ gas. The pH is controlled by the addition of caustic, lime, or acid to the solution. In most cases, a slightly or moderately alkaline pH is used, depending on the type of oxidizing agent being used and the compound being treated (see Section 19.2, Underlying Principles of Operation). In alkaline chlorination treatment of organics, a slightly acidic pH may be selected as an optimum. In permanganate oxidation, a pH of 2 to 4 is often selected. EPA monitors the pH continuously, if possible, to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

### 19.5.5 Oxidation Temperature

Temperature affects the rate of reaction and the solubility of the oxidizing agent in the waste. As the temperature is increased the solubility of the oxidizing agent, in most instances, is increased and the required residence time, in most cases, is reduced. EPA monitors the oxidation temperature continuously, if possible, to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

### 19.5.6 Amount and Type of Catalyst

Adding a catalyst that promotes oxygen transfer and thus enhances oxidation has the effect of lowering the necessary reactor temperature and/or improving the level of destruction of oxidizable compounds. For waste constituents that are more difficult to oxidize, catalyst addition may be necessary to effectively destroy the constituent(s) of concern. Catalysts typically used for this purpose include copper bromide and copper nitrate. If a catalyst is required, EPA examines the amount and type added, as well as the method of addition of the catalyst to the waste, to ensure that effective oxidation is achieved.

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# 20. POLISHING FILTRATION

## 20.1 Applicability

Polishing filtration is a treatment technology applicable to wastewaters containing relatively low concentrations of solids (less than 1,000 mg/l). This type of filtration is typically used as a polishing step for the supernatant liquid following chemical precipitation and settling/clarification of wastewaters containing metal and other inorganic precipitates. Polishing filtration removes particles that are difficult to settle because of their shape and/or density, as well as precipitated particles from an underdesigned settling system.

## 20.2 Underlying Principles of Operation

The basic principle of operation for polishing filtration is the removal of particles from a mixture of fluid and particles by a medium that permits the flow of the fluid but retains the particles. The larger the particles, the easier they are to remove from the fluid.

Extremely small particles, in the colloidal range, may not be removed effectively in a polishing filtration system and thus may appear in the treated wastewater. To mitigate this problem, the wastewater can be treated prior to filtration to modify the particle size distribution in favor of the larger particles by using appropriate precipitants, coagulants, flocculants, and filter aids. The selection of the appropriate precipitant and coagulant is important because they affect the type of waste particles formed. For example, lime precipitation usually produces larger, less gelatinous particles (which are easier to remove from aqueous wastes using this technology) than does caustic soda precipitation. For particles that become too small to remove effectively because of poor resistance to shearing, the use of coagulants and flocculants both improves shear resistance and increases the size of the particles. Also, if pumps are used, shear can be minimized by lowering the pump speed or using a low-shear type of pump. Filter aids such as diatomaceous earth are used to precoat cloth-type filter media and to provide an initial filter cake onto which additional solids can be deposited during the filtration process. The presence of the precoat aids in the removal of small particles from the solution being filtered. These particles adhere to the precoat solids during the filtration process.

## 20.3 Description of Polishing Filtration Processes

During polishing filtration, wastewater may flow by gravity or under pressure to the filter. The two most common polishing filtration processes are cartridge and granular bed filtration. Both processes remove particles that are much smaller than the pore size of the filter media by straining, adsorption, and coagulation/flocculation mechanisms; they are also capable of producing an effluent with a low level of solids (less than 10 mg/l).

### 20.3.1 Cartridge Filtration

Cartridge filters can be used for relatively low waste feed flows. In this process, a cylindrically shaped cartridge with a matted cloth-type filter medium, is placed within a sealed vessel. Wastewater is pumped through the cartridge until the flow drops excessively or until the pumping pressure becomes too high because of plugging of the filter media. The sealed vessel is then opened and the plugged cartridge is removed and replaced with a new cartridge. The plugged cartridge is then disposed of. Cartridge filters may be assembled in a parallel arrangement to increase the overall system flow.

### 20.3.2 Granular Bed Filtration

For relatively large volume flows, granulated media such as sand or anthracite coal are used singly or in combination to trap suspended solids within the pore spaces of the media. Dual and multimedia filter arrangements allow higher flow rates and efficiencies. Typical hydraulic loading rates range from 2 to 5 gal/sq ft-min for single-medium filters and from 4 to 8 gal/sq ft-min for multimedia filters.

In this process, wastewater is either gravity fed or pumped through the granular bed media and filtered until either the flow drops excessively or the pumping pressure becomes too high because of plugging of the filter media. Granular media filters are cleaned by backwashing with filtered water in an upflow manner to expand the bed, loosen the media granules, and resuspend the entrapped filtered solids. The backwash water, which may be as much as 10 percent of the volume of the filtered wastewater, is then returned to the wastewater treatment system so that the filtered solids in the backwash water can be settled out of solution prior to discharge.

## 20.4 Waste Characteristics Affecting Performance (WCAPs).

In determining whether polishing filtration will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the solid waste particle size and (b) the type of solid waste particles.

### 20.4.1 Solid Waste Particle Size

Extremely small particles, in the colloidal range, may not be filtered effectively in a polishing filter and thus may appear in the filtrate. If the solid waste particle size distribution of an untested waste is significantly lower than that of the tested waste, the system may not achieve the same performance. Pretreatment of the waste with coagulants and flocculants may be required to increase the particle sizes and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 20.4.2 Type of Solid Waste Particles

Some solids formed during metal precipitation are gelatinous in nature and are difficult to filter. In most cases, solids can be made less gelatinous by use of the appropriate coagulants and coagulant dosage prior to settling/clarification, or after settling/clarification but prior to filtration. In addition, the use of lime instead of caustic in chemical precipitation of metals reduces the formation of gelatinous solids. If solids in an untested waste are significantly more gelatinous than in the tested waste, the system may not achieve the same performance. Pretreatment of the waste with coagulants may be required to decrease the gelatinous nature of the waste and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 20.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a polishing filtration system, EPA examines the following parameters: (a) the type and size of the filter; (b) the filtration pressure; (c) the amount and type of coagulants, flocculants, and filter aids used; (d) the hydraulic loading rate; and (e) the pore size of the filter media.

### 20.5.1 Type and Size of Filter

The type and size of the polishing filtration system used is dependent on the nature of the particles to be removed, the desired solids concentration in the filtrate, and the amount and concentration of solids in the feed. As noted earlier, cartridge filtration is limited to lower volume wastewaters and/or those with lower solids concentrations than is granular bed filtration. For granular bed filtration, when more than one medium is used (dual and multimedia filter arrangements such as sand and anthracite coal), a higher capacity can be expected for the same size filter bed. For both filtration processes, the larger the filter size, the greater its hydraulic capacity (overall throughput) and the longer the filter runs between solids removal. EPA examines the type and size of the filter chosen to ensure that it is capable of achieving effective filtration of the wastewater.

### 20.5.2 Filtration Pressure

Pressure impacts both the design pore size of the filter media and the design feed flow rate (hydraulic loading rate). The higher the feed pressure, the longer the run will be prior to solids removal. For gelatinous solids, such as metal hydroxides, however, excessive pressure may cause the solids to clog the filter pores and prevent additional polishing filtration. Also, high pressures may force particles through the filter medium, resulting in ineffective filtration. EPA monitors the filtration pressure applied to the waste feed continuously, if possible, to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

### 20.5.3 Amount and Type of Coagulants, Flocculants, and Filter Aids

Coagulants, flocculants, and filter aids may be mixed with the wastewater prior to filtration. Coagulants and flocculants affect the type and size of waste particles in the wastewater and, hence, their ease of removal. Filter aids both improve the effectiveness of filtering gelatinous particles and increase the time that the filter can stay on-line by increasing the surface area available for filtration. Coagulants, flocculants, and filter aids are particularly useful when the wastewater contains a high percentage of very small particles and/or when the concentration of solids in the wastewater is low. Inorganic coagulants include alum, ferric sulfate, and lime; organic flocculants are polyelectrolytes. Diatomaceous earth is the most commonly used filter aid. The use of coagulants, flocculants, and filter aids significantly increases the amount of solids requiring removal and disposal. Polyelectrolyte flocculant usage, however, usually does not increase the solids volume significantly because the required dosage is relatively low. If the addition of coagulants, flocculants, and filter aids is required, EPA examines the amount and type added, as well as their method of addition to the wastewater, to ensure effective filtration.

### 20.5.4 Hydraulic Loading Rate

Lower hydraulic loading rates generally improve filtration performance. Higher hydraulic loading rates yield greater throughput, but result in shorter cycle times. EPA monitors the hydraulic loading rate to ensure effective filtration of the wastewater.

### 20.5.5 Pore Size of the Filter Media

The pore size of the filter media determines the particle size that will be effectively removed from the wastewater. EPA examines the pore size of the filter media to ensure effective filtration of the wastewater.

## 20.6 References

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# 21. SLUDGE FILTRATION

## 21.1 Applicability

Sludge filtration, also known as sludge dewatering or cake-formation filtration, is a technology used on wastes that contain high concentrations of suspended solids, generally higher than 1 percent (10,000 mg/l). Sludge filtration is commonly applied to waste sludges, such as clarifier solids, for dewatering. These sludges can be dewatered to 20 to 50 percent solids concentration using this technology.

## 21.2 Underlying Principles of Operation

The basic principle of operation for sludge filtration is the separation of particles from a mixture of fluid and particles by a medium that permits the flow of the fluid but retains the particles. The larger the particles, the easier they are to separate from the fluid.

Extremely small particles, in the colloidal range, may not be filtered effectively in a sludge filtration system and may appear in the filtrate. To mitigate this problem, the waste can be treated prior to filtration to modify the particle size distribution in favor of the larger particles by using appropriate precipitants, coagulants, flocculants, and filter aids. The selection of the appropriate precipitant and coagulant is important because they affect the type of waste particles formed. For example, lime precipitation usually produces larger, less gelatinous particles (which are easier to separate from waste sludges using this technology) than caustic soda precipitation. For particles that become too small to filter effectively because of poor resistance to shearing, the use of coagulants and flocculants improves shear resistance in addition to increasing the size of the particles. Also, if pumps are used, shear can be minimized by lowering the pump speed or using a low-shear type of pump. Filter aids such as diatomaceous earth are used to precoat cloth-type filter media and provide an initial filter cake onto which additional solids can be deposited during the filtration process. The presence of the precoat aids in the removal of small particles from the waste being filtered. These particles adhere to the precoat solids during the filtration process.

## 21.3 Description of Sludge Filtration Process

For sludge filtration, waste is pumped through a cloth-type filter medium (also known as pressure filtration, such as that performed with a plate and frame filter), drawn by vacuum through the cloth medium (also known as vacuum filtration, such as that performed with a vacuum drum filter), or gravity-drained and mechanically pressured through two continuous fabric belts (also known as belt filtration, such as that performed with a belt filter press). In all cases, the solids "cake" builds up on the filter medium and acts as a filter for subsequent solids removal. For a plate and frame type filter, removal of the solids is accomplished by taking the unit off-line, opening the filter, and using an adjustable knife mechanisms to scrape the solids off (a batch process). For the vacuum filter, cake is removed continuously by using an adjustable knife mechanism to scrape scraping the sludge from the vacuum drum as the drum rotates. For the belt filter, the cake is continuously removed by a discharge roller and blade, which dislodge the cake from the belt. For a specific sludge, the plate and frame type filter will usually produce the driest cake (highest percentage of solids). The belt filter produces a drier cake than a vacuum filter, but not as dry as that produced by a plate and frame filter. Dewatered solids are further treated in processes such as incineration and solvent extraction, if treatable levels of organics are present, stabilization (if treatable levels of leachable metals are present), are/or disposal.

the liquid filtrate is further treated in processes such as polishing filtration, carbon adsorption and aerobic biological treatment, and/or disposal.

## 21.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether sludge filtration will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the solid waste particle size and (b) the type of solid waste particles.

### 21.4.1 Solid Waste Particle Size

The smaller the particle size, the more the particles tend to go through the filter media. This is especially true for a vacuum filter. For a pressure filter (such as a plate and frame), smaller particles may require higher pressures for equivalent fluid throughput because the smaller pore spaces between particles collected on the filter medium create resistance to flow. If the solid waste particle size distribution of an untested waste is significantly lower than that of the tested waste, the system may not achieve the same performance. Pretreatment of the waste with coagulants and flocculants may be required to increase the particle sizes and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 21.4.2 Type of Solid Waste Particles

Some solids formed during metal precipitation are gelatinous in nature and cannot be dewatered well by sludge filtration. In fact, for vacuum filtration a cake may not form at all. In most cases, solids can be made less gelatinous by use of the appropriate coagulants and coagulant dosage prior to settling/ clarification or after settling/ clarification but prior to filtration. In addition, the use of lime instead of caustic in chemical precipitation of metals reduces the formation of gelatinous solids. Also, adding filter aids, such as lime or diatomaceous earth, to a gelatinous sludge increases its filterability significantly. Finally, precoating the filter with diatomaceous earth prior to sludge filtration assists in dewatering gelatinous sludges. If an untested waste is significantly more gelatinous than the tested waste, the system may not achieve the same performance. Pretreatment of the waste with coagulants and filter aids or precoating of the filter may be required to decrease the gelatinous nature of the waste and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 21.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a sludge filtration system, EPA examines the following parameters: (a) the type and size of filter; (b) the filtration pressure; (c) the amount and type of coagulants, flocculants, and filter aids used; and (d) the hydraulic loading rate.

### 21.5.1 Type and Size of Filter

The type and size of the filtration system used is dependent on the nature of the particles to be separated, the desired solids concentration in the cake, the amount and concentration of solids in the feed, and the required downtime for solids removal and maintenance. Typically, a pressure-type filter (such as a plate and frame) will yield a drier cake than a belt or vacuum type filter and will also be more tolerant of variations in influent sludge characteristics. Pressure-type filters, however, are batch processes. When cake is built up to the maximum depth physically possible (constrained by filter geometry) or to the maximum design pressure, the filtration system is taken off-line while the cake is removed. (An alternate unit can be put on-line while the other is being cleaned.) Belt and vacuum type filters are continuous systems (i.e., cake discharges continuously), but each of these filters is usually much larger than a pressure filter with the same capacity.

For all filter types, the larger the filter, the greater its hydraulic capacity (overall throughput) and, for pressure-type filters, the longer the filter runs between cake discharges. EPA examines the type and size of the filter chosen to ensure that it is capable of achieving effective dewatering and filtration of the waste sludge.

### 21.5.2 Filtration Pressure

Pressure impacts both the design pore size of the filter media and the design feed flow rate. For plate and frame filters, the higher the feed pressure, the drier the cake will be and the longer the runs will be prior to cake discharge. However, for gelatinous solids, such as some metal hydroxides, excessive pressures may cause the solids to clog the filter pores and prevent additional sludge filtration. Also, high pressures may force particles through the filter medium, resulting in ineffective filtration. For vacuum filters, the maximum amount of vacuum typically applied ranges from 20 to 25 inches of mercury. (The absolute maximum amount of vacuum that can be applied is 29.9 inches of mercury, or atmospheric pressure.) For belt filters, neither pressure nor vacuum is applied to the waste feed (although mechanical pressure is applied). For plate and frame and vacuum-type filtration systems, EPA monitors the filtration pressure (or vacuum) applied to the waste feed continuously, if possible, to ensure that the system is operating at the appropriate design conditions and to diagnose operational problems.

### 21.5.3 Amount and Type of Coagulants, Flocculants, and Filter Aids

Coagulants, flocculants, and filter aids may be mixed with the waste feed prior to filtration. Coagulants and flocculants affect the type and size of waste particles in the waste and, hence, their ease of removal. Their effect is particularly significant for vacuum filtration since they may make the difference between no cake and the formating of a relatively dry cake. In a pressure filter, coagulants, flocculants, and filter aids significantly improve overall throughput and cake dryness. Filter aids, such as diatomaceous earth, can be precoated on all filters for particularly difficult-to-filter sludges (those containing a high concentration of gelatinous solids). The precoat layer acts somewhat like a filter in that sludge solids are trapped in the precoat pore spaces. Coagulants, flocculants, and filter aids are particularly useful when the sludge has a high percentage of very small particles and/or when the concentration of solids in the waste feed is low. Inorganic coagulants include alum, ferric sulfate, and lime. Organic flocculants are polyelectrolytes. Diatomaceous earth is the most commonly used filter aid. The use of coagulants, flocculants, and filter aids significantly increases the amount of solids in the sludge requiring disposal, although, polyelectrolyte flocculant usage usually does not increase sludge volume significantly because the required dosage is relatively low. If the addition of coagulants, flocculants, and filter aids is required, EPA examines the amount and type added to the waste sludge, along with their method of addition, and to ensure effective dewatering and filtration.

### 21.5.4 Hydraulic Loading Rate

Lower hydraulic loading rates generally improve filtration performance. Higher hydraulic loading rates yield greater overall throughput, but result in the formation of wetter cakes (lower percent solids) and, for plate and frame filters, shorter cycle times. EPA monitors the hydraulic loading rate to ensure effective dewatering and filtration of the waste sludge.

## 21.6 References

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Eckenfelder, W.W., Jr., Patoczka, J., and Watkins, A. 1985. Wastewater treatment, Chemical Engineering. September 2, 1985.

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Perry, R. H., and Chilton, C. H. 1973. Chemical engineers'handbook. 5th ed., Section 19. New York: McGraw Hill Book Co.

# 22. THERMAL DRYING

## 22.1 Applicability

Thermal drying is a treatment technology applicable to solid wastes having a filterable solids content of approximately 40 percent or greater. Thermal drying removes water and volatile organics from a solid waste through evaporation. Thermal dryers operate in the range of 300 to 700°F and usually have mechanical agitation to improve heat transfer. Use of this technology results in a smaller volume of waste with reduced concentrations of water and volatile organics.

## 22.2 Underlying Principles of Operation

The basic principle of operation for drying is the removal of a liquid from a solid waste by evaporation. Liquid constituents will vaporize as a result of heat absorbed. In any drying process, assuming an adequate supply of heat, the rate at which liquid evaporation occurs depends on the thermal conductivity of the solid waste to be dried and the boiling points of the volatile liquid constituents to be evaporated.

## 22.3 Description of Thermal Drying Process

A wide range of batch and continuous dryers is available. One commonly used continuous-type, the screw-flight dryer, is described below.

The screw-flight dryer consists of a hollow screw and shaft enclosed in a jacketed trough. Transfer fluid is heated to temperatures as high as 750°F and circulated, usually countercurrently, through the hollow screw and shaft. Heat transfers from the screw and shaft into the feed material, causing water and organics to be driven off in a vapor form. The dried cake is discharged from the dryer.

The screw is designed to create good contact between the shaft and feed material. The screw is also equipped with breaker bars to ensure proper shearing of the input materials and to prevent the screw surfaces from fouling.

Vapors emerging from this system are managed in one of two ways, depending on their composition. If the vapors contain only water, they are directly vented to the atmosphere; however, if the vapors contain volatile organics, they are generally passed through a water-cooled condenser system. The recovered organic liquids from the condenser unit are then forwarded to another process for treatment or recovery.

## 22.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether thermal drying will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the thermal conductivity of the waste and (b) the volatile liquid constituent boiling points.

### 22.4.1 Thermal Conductivity of the Waste

A major factor determining whether a particular constituent will volatilize is the transfer of heat through the waste. For thermal drying, heat transfer is accomplished by both convection and conduction.

EPA examined both methods of heat transfer and believes that conduction would be the primary cause of heat transfer differences between wastes. Heat flow by conduction is proportional to the temperature gradient across the material. The proportionality constant is referred to as the thermal conductivity and is a property of the material to be dried. With regard to convection, EPA believes that the amount of heat transferred by convection will generally be more a function of the system design than of the waste itself.

Thermal conductivity measurements, as part of a treatability comparison for two different wastes to be treated by a single dryer unit, are most meaningful when applied to wastes that are homogeneous (i.e., uniform throughout). As wastes exhibit greater degrees of nonhomogeneity, thermal conductivity becomes less accurate in predicting treatability because the measurement essentially reflects heat flow through regions having the greatest conductivity (i.e., the path of least resistance) and not heat flow through all parts of the waste. Nevertheless, EPA believes that thermal conductivity may provide the best measure of performance transfer. If the thermal conductivity of an untested waste is significantly lower than that of the tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 22.4.2 Volatile Liquid Constituent Boiling Points

The lower the boiling points of the volatile liquid constituents, the more easily they will be evaporated and the solid waste dried. If the boiling points of the volatile liquid constituents in the untested waste are significantly higher than those in the tested waste, the system may not achieve the same performance. More rigorous drying conditions including a higher temperature, lower pressure, and a longer residence time may be required to evaporate less volatile liquid constituents and achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 22.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a thermal drying system, EPA examines the following parameters: (a) the drying temperature and pressure and (b) the residence time.

### 22.5.1 Drying Temperature and Pressure

Temperature provides an indirect measure of the energy available (i.e., Btu/hr) to vaporize the waste constituents. As the design temperature increases, more constituents with lower volatilities will be removed from the waste.

Pressure is integrally related to the boiling point of the waste and the subsequent vaporization of the water and/or organic constituents. As the pressure is lowered below atmospheric (i.e., as vacuum is increased), the boiling point of the waste will also be lowered, thereby requiring less heat input to volatilize waste constituents. EPA monitors the drying temperature as well as the pressure (if pressures other than atmospheric are used) to ensure that the system is operating at appropriate conditions and to diagnose operational problems.

### 22.5.2 Residence Time

The residence time determines the necessary energy input into the system as well as the degree of volatilization of water and volatile organics. It is dependent on the dryer temperature and the thermal conductivity of the waste. EPA observes the residence time to ensure that the treatment system provides sufficient time to effectively evaporate the volatile liquid constituents and, hence, dry the solid waste.

## 22.6 References

Perry, R.H., and Chilton, C.H. 1973. Chemical engineers' handbook. 5th ed. New York: McGraw-Hill Book Co.

Risk Sciences International. 1987. Evaluation of treatment technologies for listed petroleum industry wastes. Interim Report. pp. 41-45.

# 23. WET AIR OXIDATION

## 23.1 Applicability

Wet air oxidation is a treatment technology applicable to wastewaters containing organics and oxidizable inorganics such as cyanide. The process is typically used to oxidize sewage sludge, regenerate spent activated carbon, and treat process wastewaters. Wastewaters treated using this technology include pesticide wastes, petrochemical process wastes, cyanide-containing metal finishing wastes, spent caustic wastewaters containing phenolic compounds, and some organic chemical production wastewaters.

This technology differs from other treatment technologies generally used to treat wastewaters containing organics in several ways. First, wet air oxidation can be used to treat wastewaters that have higher organic concentrations than are normally handled by biological treatment, carbon adsorption, and chemical oxidation, but may be too dilute to be effectively treated by thermal processes such as incineration. Wet air oxidation is most applicable for waste streams containing dissolved or suspended organics in the 500 to 15,000 mg/l range. Below 500 mg/l, the rates of wet air oxidation of most organic constituents are too slow for efficient application of this technology. For these more dilute waste streams, biological treatment, carbon adsorption, or chemical oxidation may be more applicable. For more concentrated waste streams (above 15,000 mg/l), thermal processes such as incineration may be more applicable. Second, wet air oxidation can be applied to wastes that have significant concentrations of metals (roughly 2 percent), whereas biological treatment, carbon adsorption, and chemical oxidation may have difficulty in treating such wastes.

It is important to point out that wet air oxidation proceeds by a series of reaction steps and the intermediate products formed are not always as readily oxidized as are the original constituents. Therefore, the process does not always achieve complete oxidation of the organic constituents. Accordingly, in applying this technology it is important to assess potential products of incomplete oxidation to determine whether further treatment is necessary or whether this technology is appropriate at all.

Studies of the wet air oxidation of different compounds have led to the following empirical observations concerning a compound's susceptibility to wet air oxidation based on its chemical structure:

1. Aliphatic compounds, even with multiple halogen atoms, can be destroyed within conventional wet air oxidation conditions. Oxygenated compounds (such as low molecular weight alcohols, aldehydes, ketones, and carboxylic acids) are formed, but these compounds are readily biotreatable.

2. Aromatic hydrocarbons, such as toluene, acenaphthene, or pyrene, are easily oxidized.

3. Halogenated aromatic compounds can be oxidized provided there is at least one nonhalogen functional group present on the ring (e.g., pentachlorophenol (-OH) or 2,4,6-trichloroaniline ($-NH_2$)).

4. Halogenated aromatic compounds, such as 1,2-dichlorobenzene, and PCBs, such as Aroclor 1254, are resistant to wet air oxidation under conventional conditions.

5. Halogenated ring compounds, such as the pesticides aldrin, dieldrin, and endrin, are expected to be resistant to conventional wet air oxidation.

6. DDT can be oxidized, but results in the formation of intractable oils in conventional wet air oxidation.

7. Heterocyclic compounds containing oxygen, nitrogen, or sulfur are expected to be destroyed by wet air oxidation because the O, N, or S atoms provide a point of attack for oxidation reactions to occur.

## 23.2 Underlying Principles of Operation

The basic principle of operation for wet air oxidation is that the enhanced solubility of oxygen in water at high temperatures and pressures aids in the oxidation of organics. The typical operating temperature for the wet air oxidation treatment process ranges from 175 to 325°C (347 to 617°F). The pressure is maintained at a level high enough to prevent excessive evaporation of the liquid phase at the operating temperature, generally between 300 and 3000 psi. At these elevated temperatures and pressures, the solubility of oxygen in water is dramatically increased, thus providing a strong driving force for the oxidation. The reaction must take place in the aqueous phase because the chemical reactions involve both oxygen (oxidation) and water (hydrolysis). The wet air oxidation process for a specific organic compound generally involves a number of oxidation and hydrolysis reactions in series, which degrade the initial compound by steps into a series of compounds of simpler structure. Complete wet air oxidation results in the conversion of organic compounds into carbon dioxide, water vapor, ammonia (for nitrogen-containing wastes), sulfate (for sulfur-containing wastes), and halogen acids (for halogenated wastes).

However, treatable quantities of partial degradation products may remain in the treated wastewaters from wet air oxidation. Therefore, effluents from wet air oxidation processes may be given subsequent treatment including biological treatment, carbon adsorption, or chemical oxidation before being discharged.

## 23.3 Description of Wet Air Oxidation Process

A conventional wet air oxidation system consists of a high-pressure liquid feed pump, an oxygen source (air compressor or liquid oxygen vaporizer), a reactor, heat exchangers, a vapor-liquid separator, and process regulators. A basic flow diagram is shown in Figure 23-1.

A typical batch wet air oxidation process proceeds as follows. First, a copper catalyst solution may be mixed with the aqueous waste stream if preliminary testing indicates that a catalyst is necessary. The waste is then pumped into the reaction chamber. The aqueous waste is pressurized and heated to the design pressure and temperature, respectively. After reaction conditions have been established, air is fed to the reactor for the duration of the design reaction time. At the completion of the wet air oxidation process, suspended solids or gases are removed and the remaining treated aqueous waste is either discharged directly to disposal or fed to a biological treatment, carbon adsorption, or chemical oxidation treatment system if further treatment is necessary prior to discharge to disposal.

Wet air oxidation can also be operated in a continuous process. In continuous operation, the waste is pressurized, mixed with pressurized air or oxygen, preheated in a series of heat exchangers by the hot reactor effluent and steam, and fed to the reactor. The waste feed flow rate controls the reactor residence time. Steam is fed into the reactor column to adjust the column temperature. The treated waste is separated

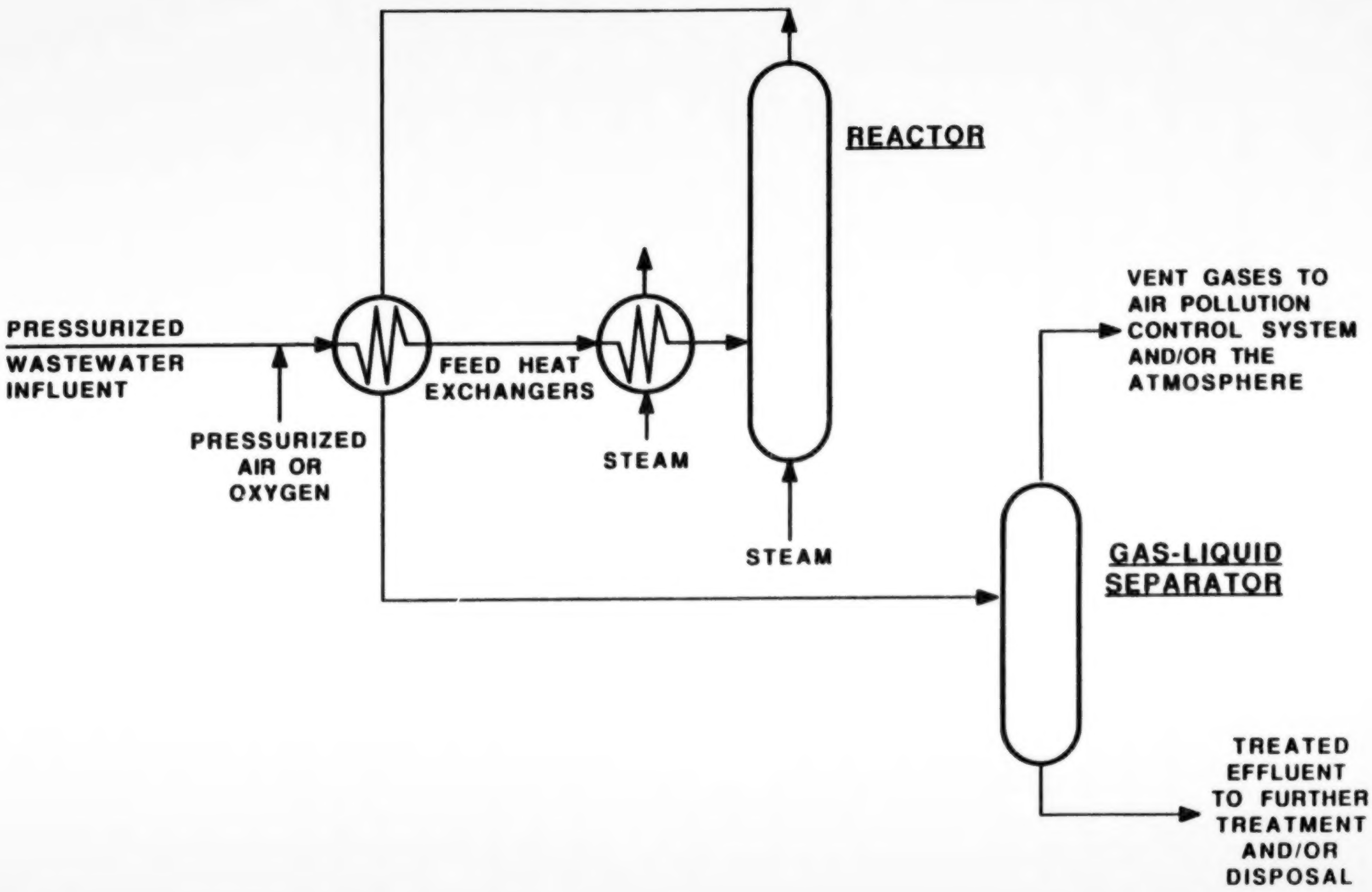
PRESSURIZED WASTEWATER INFLUENT
PRESSURIZED AIR OR OXYGEN
FEED HEAT EXCHANGERS
STEAM
STEAM
REACTOR
VENT GASES TO AIR POLLUTION CONTROL SYSTEM AND/OR THE ATMOSPHERE
GAS-LIQUID SEPARATOR
TREATED EFFLUENT TO FURTHER TREATMENT AND/OR DISPOSAL

Figure 23-1. Continous Wet Air Oxidation System.

in a gas-liquid separator, with the gases treated in an air pollution control system and/or discharged to the atmosphere, and the liquids either further treated, as mentioned above, and/or discharged to disposal.

## 23.4 Waste Characteristics Affecting Performance (WCAPs)

In determining whether wet air oxidation will achieve the same level of performance on an untested waste as on a previously tested waste and whether performance levels can be transferred, EPA examines the following waste characteristics: (a) the chemical oxygen demand and (b) the concentration of interfering substances.

### 23.4.1 Chemical Oxygen Demand

The chemical oxygen demand (COD) of the waste is a measure of the oxygen required for complete oxidation of the oxidizable waste constituents. The limit to the amount of oxygen that can be supplied to the waste is dependent on the solubility of oxygen in the aqueous waste and the rate of dissolution of oxygen from the gas phase to the liquid phase. This sets an upper limit on the amount of oxidizable compounds that can be treated by wet air oxidation. Thus, high-COD wastes may require dilution for effective treatment to occur. If the COD of the untested waste is significantly higher than that of the tested waste, the system may not achieve the same performance. Pretreatment of the waste or dilution as part of treatment may be needed to reduce the COD to within levels treatable by the dissolved oxygen concentration and to achieve the same treatment performance, or other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

### 23.4.2 Concentration of Interfering Substances

In some cases, addition of a water-soluble copper salt catalyst to the waste before processing is necessary for efficient oxidation treatment (for example, for oxidation of some halogenated organics). Other metals have been tested and have been found to be less effective. Interfering substances for the wet air oxidation process are essentially those that cause the formation of insoluble copper salts when copper catalysts are used. To be effective in catalyzing the oxidation reaction, the copper ions must be dissolved in solution. Sulfide, carbonate, and other negative ions that form insoluble copper salts may interfere with treatment effectiveness if they are present in significant concentrations in wastes for which copper catalysts are necessary for effective treatment. If an untested waste for which a copper catalyst is necessary for effective treatment has a concentration of interfering substances (including sulfide, carbonate, or other anions that form insoluble copper salts) significantly higher than that in a tested waste, the system may not achieve the same performance and other, more applicable treatment technologies may need to be considered for treatment of the untested waste.

## 23.5 Design and Operating Parameters

In assessing the effectiveness of the design and operation of a wet air oxidation system, EPA examines the following parameters: (a) the oxidation temperature, (b) the residence time, (c) the excess oxygen concentration, (d) the oxidation pressure, and (e) the amount and type of catalyst.

### 23.5.1 Oxidation Temperature

Temperature is the most important parameter affecting the system. The design temperature must be high enough to allow the oxidation reactions to proceed at acceptable rates. Raising the temperature increases the wet air oxidation rate by enhancing oxygen solubility and oxygen diffusivity. The process is normally operated in the temperature range of 175 to 325°C (347 to 617°F), depending on the hazardous constituent(s) to be treated. EPA monitors the oxidation temperature continuously, if possible, to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

### 23.5.2 Residence Time

The residence time impacts the extent of oxidation of waste contaminants. For a batch system, the residence time is controlled directly by adjusting the treatment time in the reaction tank. For a continuous system, the waste feed rate is controlled to make sure that the system is operated at the appropriate design residence time. Generally, the reaction rates are relatively fast for the first 30 minutes and become slow after 60 minutes. Typical residence times, therefore, are approximately 1 hour. EPA monitors the residence time to ensure that sufficient time is provided to effectively oxidize the waste.

### 23.5.3 Excess Oxygen Concentration

The system must be designed to supply adequate amounts of oxygen for the compounds to be oxidized. An estimate of the amount of oxygen needed can be made based on the COD content of the untreated waste; excess oxygen should be supplied to ensure complete oxidation. The source of oxygen is compressed air or a high-pressure pure oxygen stream. EPA monitors the excess oxygen concentration (the concentration of oxygen in the gas leaving the reactor) continuously, if possible, by sampling the vent gas from the gas-liquid separator to ensure that an effective amount of oxygen or air is being supplied to the waste.

### 23.5.4 Oxidation Pressure

The design pressure must be high enough to prevent excessive evaporation of water and volatile organics at the design temperature. This allows the oxidation reaction to occur in the aqueous phase, thereby improving treatment effectiveness. EPA monitors the oxidation pressure continuously, if possible, to ensure that the system is operating at the appropriate design condition and to diagnose operational problems.

### 23.5.5 Amount and Type of Catalyst

Adding a catalyst that promotes oxygen transfer and thus enhances oxidation has the effect of lowering the necessary reactor temperature and/or improving the level of destruction of oxidizable compounds. For waste constituents that are more difficult to oxidize, the addition of a catalyst may be necessary to effectively destroy the constituent(s) of concern. Catalysts typically used for this purpose include copper bromide and copper nitrate. If a catalyst is required, EPA examines the amount and type added, as well as the method of addition of the catalyst to the waste, to ensure that effective oxidation is achieved.

## 23.6 References

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# B. HIGH-TEMPERATURE STABILIZATION TECHNOLOGIES

## B.1 Applicability

High-temperature stabilization technologies include glass and slag vitrification and elevated-temperature calcination processes. Vitrification processes involve dissolving of the waste at high temperatures into glass or a glasslike matrix. Calcination involves merely heating of the material at high temperatures.

High-temperature vitrification is applicable to nonwastewaters containing arsenic* or other EP toxic metal constituents that are relatively nonvolatile at the temperatures at which the process is operated. It is also applicable to many wastes containing organometallic compounds, where the organic portion of the compound can be completely oxidized at process-operating conditions.

The process is not applicable to volatile metallic compounds or to wastes containing high levels of constituents that will interfere with the vitrification process. High levels of chlorides and other halogen salts should be avoided in the wastes being processed because they interfere with glassmaking processes and cause corrosion problems.

Calcination processes are applicable to inorganic wastes that do not contain volatile constituents.

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* Volatile arsenic compounds are generally converted to nonvolatile arsenate salts such as calcium arsenate prior to use of this process. In ordinary glassmaking, arsenic volatilization problems are minimized by adding arsenic as arsenate salts.

## B.2 Underlying Principles of Operation

The basic principles of operation for high-temperature stabilization technologies are dependent on the technology used. In glass and slag vitrification processes, the waste constituents become chemically bonded inside a glasslike matrix in many cases. In all instances, the waste becomes surrounded by a glass matrix. This acts to immobilize the waste constituents and to retard or prevent their reintroduction into the environment. Arsenates are converted to silicoarsenates, and other metals are converted to silicates.

High-temperature calcination processes remove water of hydration from the toxic metal-bearing solids, convert hydroxides present to oxides, and sinter the material, reducing its surface area to a minimum. Conversion of hydroxides to oxides and minimization of available surface area retard surface reactions that would reintroduce the material into the environment. Calcination may also be accompanied by chemical reaction if a material such as lime is blended with the waste before it is heated. For example, lime will react with arsenic oxides at higher temperatures to form calcium arsenate, and this material will then be sintered at elevated temperatures. Brief descriptions of each of the high-temperature processes are given below.

### B.2.1 Glass Vitrification

In the glass vitrification process, the waste and normal glassmaking constituents are first blended together and then fed to a glassmaking furnace, where the mixed feed materials are introduced into a pool of molten glass. The feed materials then react with each other to form additional molten glass, in which particles of the waste material become dissolved or suspended. The molten glass is subsequently cooled. As it cools, it solidifies into a solid mass that contains the dissolved and/or suspended waste constituents. Entrapment and chemical bonding within the glass matrix renders the waste constituents unavailable for reaction.

### B.2.2 Slag Vitrification

Slag vitrification differs from glass vitrification in that finely ground slag from metal-refining processes and waste are premixed and fed to the same type of furnace as that used for glassmaking. The slag liquifies at the process temperature (1100 to 1200°C), and the waste constituents either dissolve or become suspended in the molten slag. Subsequent cooling of the slag causes it to solidify, trapping the waste inside a glasslike matrix and rendering it unavailable for chemical reaction or migration into the environment.

### B.2.3 High-Temperature Calcination

In the high-temperature calcination process, the waste is heated in a furnace or kiln to between 400 and 800°C. In some instances, the waste may be blended with lime prior to heating. In those cases, chemical reaction may occur during the calcining process. Water present as either free water or water of hydration is evaporated, and hydroxides present are thermally decomposed to the corresponding oxides and water vapor. At the higher temperatures, the surface area of the dehydrated material is decreased by thermal sintering. Conversion of hydroxides to oxides and substantial losses of surface area render the material less reactive in the environment and lower the leachability of EP toxic metals present. In general, the higher the calcination temperatures used, the more complete is the loss of water and the greater is the accompanying loss of surface area, resulting in lower leachability potential.

## B.3 Description of the High-Temperature Stabilization Processes

This chapter discusses three types of high-temperature stabilization processes, which differ considerably from each other. Individual process descriptions are given in the following subsections.

### B.3.1 Glass Vitrification

Soda ash, lime, silica, boron oxide, and other glassmaking constituents are first blended with the waste to be treated. The amount of waste added to the blend is dependent on the waste composition. Different metal oxides have differing solubility limits in glass matrices. The blended waste and glass raw material mixture is then fed to a conventional, heated glass electric furnace.

The introduced material typically is added through a port at the top of the furnace and falls into a pool of molten glass. The glass constituents dissolve in the molten glass and form additional glass. Molten glass is periodically withdrawn from the bottom of the furnace and cooled. This material then solidifies on cooling into solid blocks of glasslike material. Organics present in the feed mixture undergo combustion at the normal operating temperatures of 1100 to 1400°C and are fully oxidized to carbon dioxide and water vapor.

The top of the furnace is normally cooled so that volatile materials, such as arsenic oxides, that are present in the feed mixture condense on the cooled surface and fall back into the melt, where they can undergo chemical reaction to form silicoarsenates involved in the glassmaking process. Most of the arsenic used in making glass by this method is present as salts such as calcium arsenate. This approach was introduced into the glass industry to minimize fugitive arsenic losses.

Gases, such as carbon dioxide, that are liberated during the glassmaking process exit the furnace through the top and are generally wet-scrubbed prior to reentering the atmosphere.

### B.3.2 Slag Vitrification

The slag vitrification process is basically similar to glass vitrification except that granulated slag, instead of the normal glassmaking constituents, is blended with the waste for feed to the system. A pool of liquid slag is present in the furnace, and the blended raw material mix typically is introduced at the top of the furnace and falls into this molten slag. The granulated slag-waste mixture liquifies to form additional slag. Slag is periodically withdrawn from the slag pool and cooled into blocks.

The type of furnace used for glass vitrification can also be used for slag vitrification. The operating parameters are similar.

### B.3.3 High-Temperature Calcination

In the high-temperature calcination process, wastes containing inorganic compounds are fed to ovens or kilns, where they are heated to high temperatures (i.e., 500 to 900°C) to drive off water of hydration and to convert hydroxides present to the corresponding oxides. This process is primarily applicable to inorganic wastes that contain nonvolatile constituents.

The waste is heated in the oven or kiln to the desired temperature, moisture and water of hydration are driven off, and, at the 500 to 900°C temperature range, hydroxides decompose to the corresponding oxides and water vapor. The high-temperature treatment also significantly reduces the surface areas of the oxides formed by sintering, thereby reducing the reactivity of the material. After the waste material has been calcined at an elevated temperature, it is withdrawn from the oven or kiln, cooled, and either land disposed or forwarded to another process such as stabilization for further treatment.

## B.4 Waste Characteristics Affecting Performance (WCAPs)

The waste characteristics affecting performance are different for the two vitrification processes and the calcination process. Accordingly, they are discussed separately in the following subsections.

### B.4.1 Waste Characteristics Affecting Performance of Vitrification Processes

In determining whether vitrification will achieve the same level of performance on an untested waste as on a previously tested waste, and whether performance levels can be transferred, EPA examines the following waste characteristics that affect performance of the vitrification processes: (1) organic content of the waste, (2) concentrations of specific metal ions in the waste, (3) concentrations of compounds in the waste that interfere with the glassmaking process, and (4) moisture content of the waste.

(1) Organic content. At process operating temperatures (1100 to 1400°C), organics are combusted to carbon dioxide, water, and other gaseous products. The combustion process liberates heat, reducing the external energy requirements for the process.

The amount of heat liberated by combustion is a function of the Btu value of the waste. The Btu content merely changes the energy input needs for the process and does not affect waste treatment performance. The amount of material that may not oxidize completely is a function of the organic halogen content of the waste. The presence of these halogenated organics does impact process performance because sodium chloride has a low solubility in glass. The presence of high chlorides results in a porous glass that is undesirable. If the halogenated organic content of an untested waste is the same as or less than that present in an already tested waste, the system should achieve the same performance for organic destruction.

(2) Concentrations of specific metal ions. Most metal oxides have solubility limits in glass matrices. Hence, their concentration determines the amount of glass-forming materials or slag with which they must be reacted in this process to generate a nonleaching slag or glass. The solubility limits of most common metal oxides and salts in glass are found in the Handbook of Glass Manufacture and other treatises on glass production. Oxides for which extensive solubility information is available are alumina, antimony oxide, arsenic oxides, barium oxide, cadmium oxide, chromium oxides, copper oxides, cobalt oxides, iron oxides, lead oxides, manganese oxides, nickel oxides, selenium oxides, tin oxides, and zinc oxides. Analysis for individual metal concentrations in the waste can be performed according to EPA-approved methods. If the concentrations of specific metals in an untested waste are less than those in a tested waste, then the same ratio of slag or glass raw materials to waste may be used for vitrification purposes. If, however, the concentration of metal is greater than that in the tested waste, a different formulation must be used.

(3) Concentrations of deleterious materials. Some waste constituents, such as chlorides, fluorides, and sulfates, interfere with the vitrification process if present at high levels. These salts have limited solubilities in glass; therefore, when they are present, additional glass-forming raw materials must be added to compensate for their presence. The solubility limits of various salts in glasses are

discussed in references on glass production such as the Handbook of Glass Manufacture. Generally, if the concentrations of such materials in an untested waste are lower than those in a tested waste, then the same ratio of glass-forming constituents to waste may be used. Reducing agents such as carbon or ferrous salts reduce arsenates and selenates to lower valence compounds that are more volatile. These properties should not be present when vitrifying arsenic or selenium.

(4) Moisture content. Materials fed to the vitrification process should be reasonably dry (i.e., contain less than 5 percent free moisture). If a waste has excess moisture above this level, it should be thermally dried before it is blended with glass-forming materials, as it may react violently when introduced to the molten glass or slag pool.

### B.4.2 Waste Characteristics Affecting Performance of High-Temperature Calcination

In determining whether high-temperature calcination will achieve the same level of performance on an untested waste as on a previously tested waste, and whether performance levels can be transferred, EPA examines the following waste characteristics that impact the performance of the high-temperature calcination process: (1) the organic content of the waste, (2) the moisture content of the waste, and (3) the inorganic composition of the waste. These characteristics are discussed below.

(1) Organic content. Calcination temperatures normally used are too low to initiate combustion of some types of organic compounds. However, they are high enough to cause volatilization of organics, which have to be removed from process off-gases. For these reasons, the presence of significant levels of organics is undesirable but can be handled with appropriate air pollution controls. Organics, per se, do not interfere with the conversion of oxides to hydroxides or with sintering processes.

(2) Moisture content. Excess water that has to be removed from the waste by heating increases the amount of time needed to bring the waste to the calcination temperature. For this reason, wastes with high moisture content should be dewatered prior to the use of this process.

(3) Inorganic composition. Calcination temperatures are normally selected based on the temperatures at which hydroxides are thermally decomposed to the corresponding oxides and water vapor. To select an optimum operating temperature, the approximate composition of the waste should be known.

A few toxic metal oxides have fairly low volatilization temperatures. Arsenic oxide, selenium dioxide, and mercuric oxide all volatilize below 500°C. High-temperature calcination should not be used for wastes that contain these volatile constituents unless they are blended with materials such as lime, which will react with them before they can vaporize. Nonvolatile arsenic compounds such as ferric and calcium arsenates may be calcined without concern for vaporization of material.

## B.5 Design and Operating Parameters

The design and operating parameters for the vitrification processes are similar to each other, but differ considerably from those for high-temperature calcination. The following subsections discuss these two technologies separately.

### B.5.1 Design and Operating Parameters for Vitrification Processes

In assessing the effectiveness of the design and operation of a vitrification system, EPA examines the following parameters: (1) the composition of the vitrifying agent, (2) the operating temperature, (3) the residence time, and (4) the vitrification furnace design.

(1) Composition of the vitrifying agent. Slag and various glassmaking formulations are used as vitrifying agents. The choice of the vitrifying agent is determined by the solubility of the waste constituents to be vitrified. Different inorganic oxides have differing solubilities in various glass matrices.

For slags, the presence of carbon or other reducing agents is undesirable when vitrifying arsenic-bearing or selenium-bearing wastes. Carbon or ferrous salts in the slag reduce arsenates in the waste to arsenic trioxide, which has a low volatilization temperature. Likewise, these same reducing agents reduce selenates to elemental selenium, which also has a low volatilization temperature. When slags are used for vitrifying arsenic-bearing and selenium-bearing wastes, EPA monitors the composition of the granulated slags to ensure that they do not contain significant concentrations of carbon or ferrous salts.

In glass vitrification, various glassmaking formulations can be used. EPA examines the proposed formulations to ensure that the toxic metal ion concentrations of the final product do not exceed solubility limits. Hence, EPA examines the material balances based on waste composition and glassmaking additives and the published solubility limits for metal oxides in various glasses to ensure that the vitrified product is indeed a glass containing the solubilized toxic waste constituents.

(2) Operating temperature. Vitrification furnaces are normally operated in the 1100 to 1400°C range. The exact operating temperature is usually selected based on the desired composition of the final product. Furnaces are normally equipped with automatic temperature control systems.

EPA examines the basis of choice for operating temperatures and the nature and physical condition of the temperature monitoring and control equipment to ensure that the system is being properly operated.

(3) Residence time. Sufficient time must be allowed for the materials added to glass furnaces to reach operating temperatures and then undergo the chemical reactions needed to produce glasses. Residence times are normally on the order of 1 to 2 hours for processes operated at 1100 to 1200°C. For glasses or slags requiring slightly higher temperatures, slightly longer residence times are usually selected. EPA examines the basis for the facility's choice of residence times to ensure that the system is well operated.

(4) Vitrification furnace design. Vitrification furnaces normally incorporate the following design features:

- Withdrawal of the product in liquid form from the base of the furnace.
- Maintenance of a liquid pool of product in the furnace.
- Addition of product constituent mix at the top of the furnace.
- Design of the top area of the furnace in a manner that allows for cooling of this area. (This is important because volatile constituents of the input feed may vaporize from the melt. The cool top area allows these constituents to condense and fall back into the melt.)
- Presence and proper operation of an air emissions control scrubbing system to manage vent gas emissions from the system such as hydrogen chloride vapors from combustion of any chlorinated organics present.

EPA examines the furnaces to be used for waste vitrification to ensure that the design features mentioned above are present, since they are important for proper operation of the systems.

## B.5.2 Design and Operating Parameters for High-Temperature Calcination Systems

In assessing the effectiveness of the design and operation of a high-temperature calcination process, EPA examines the following parameters: (1) operating temperature, (2) residence time, and (3) air emission control units in place on the ovens or kilns used.

(1) Operating temperatures. Calcination temperatures of from 500 to 900°C have been used in practice. The calcination temperature selected is generally a temperature above which metal hydroxides present will decompose to the corresponding oxides. Data on decomposition temperatures of some metal hydroxides are given in Table B-1. The temperature chosen is normally high enough to cause extensive sintering (surface area loss) of the oxides formed, while at the same time not volatilizing these materials. EPA examines the technical basis for selection of the calcining temperature to determine whether the system is properly operated. EPA also examines the temperature monitoring and control systems in place to determine whether they are properly operated and reliable.

Table B-1 Metal Hydroxide Decomposition Temperatures

| Metal hydroxide | Decomposition temperature (°C) |
|---|---|
| Cadmium hydroxide | 300 |
| Chromic acid | 400 |
| Lead hydroxide | 145 |
| Nickel hydroxide | 230 |
| Zinc hydroxide | 125 |

Source: Weast 1977.

(2) Residence time. Calcination is generally a batch process, and sufficient time must be allowed for samples to be brought to the operating temperature. Residence times of several hours are normally used to minimize the effects of heat-up time. EPA examines the technical basis for the choice of residence time to ensure that sufficient heating at the required temperature is allowed to complete the dehydration and sintering processes. Residence time is a function of the time needed to bring the calcination furnace or kiln to the desired temperature and the time needed to complete the dehydration and sintering processes at the selected temperature.

(3) Air emissions control systems. During the calcination process, water vapor is driven off as it is formed by the decomposition of hydroxides present in the waste. These hot gases exit the calcination furnace or kiln as they are formed. Some particulates of the waste material may become entrained in these vent gases; therefore, for air pollution control purposes, the calcination units must be equipped with wet or dry particulate collection systems that are properly designed and operated. EPA examines the design basis, physical condition, and maintenance of these air emissions control units to determine whether they are properly designed, maintained, and operated. EPA also examines the system of management in use for handling and subsequent treatment of the collected particulates to ensure that these finely divided waste particles are properly managed.

## B.6 References

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